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THE COMPRESSION OF 39 SUBSTANCES TO 100,000 KG/CM²

By P. W. Bridgman

ROUGH COMPRESSIONS OF 177 SUBSTANCES TO 40,000 KG/CM²

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THE COMPRESSION OF 39 SUBSTANCES TO 100,000 KG/CM²

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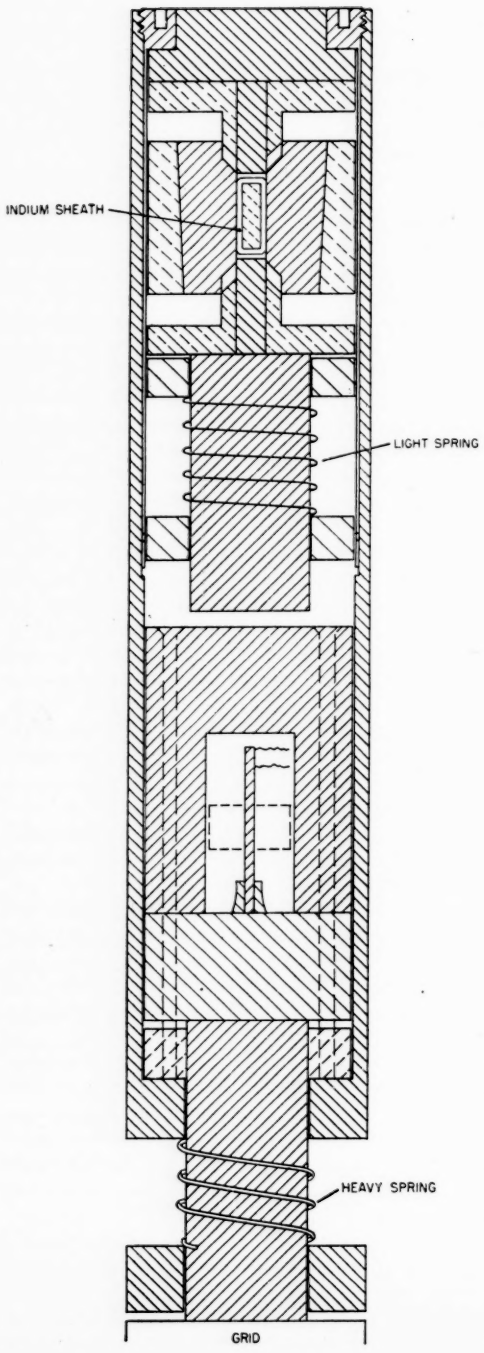
Introduction

In this paper the program of measurement of the compressions of various substances to 100,000 kg/cm² already initiated in two papers (1) is continued to 39 substances, including elements, various sulfides, selenides and tellurides, and 6 glasses. A number of improvements have been made in the apparatus, permitting somewhat greater accuracy and consequently the extension of the measurements to substances with too low a compressibility to have been previously attempted.

Apparatus and Method

The apparatus consists essentially of a miniature high pressure piezometer entirely surrounded by an outer pressure vessel containing fluid in which the pressure may be raised to 30,000 kg/cm² in order to support the miniature piezometer. Measurements are made of the force driving the pistons of the high pressure piezometer and the displacement of those pistons. Previously the force has been measured in terms of the change of electrical resistance of a compression member mounted within the pressure vessel by which the force is transmitted to the high pressure pistons, and the displacement by measuring the displacement of the piston of the external pressure vessel, which is transmitted through various intermediate members to the high pressure pistons. This latter measurement has always been more or less unsatisfactory because of the distortion of the transmitting members, which are subject to friction and hysteresis in a way not completely reproducible. The major improvement in the new apparatus consists in measuring the displacement of the high pressure pistons from the inside of the 30,000 pressure vessel, thus eliminating the irregularities due to friction and hysteresis. This has been done by attaching the pistons to a moving slide wire of the same type as that used in much of my previous work. The displacement of the wire is determined in terms of the potentiometer resistance of that portion of the wire included between a terminal fixed to the wire and a contact fixed to the rest of the apparatus over which the wire slides. The method demands three electrically insulated leads, two for the potential taps to the potentiometer, and one for the current, the other current terminal being grounded. In all, seven electrically insulated leads into the pressure vessel are now needed, three for the "grid" with which the force driving the piston is measured, one for the manganin pressure gauge, and three for the displacement. Formerly, it had not been found possible to make insulating pressure plugs which would carry more than four terminals. My mechanic, Mr. Charles E. Chase, has now found with great skill how to construct plugs with seven terminals, and this alone has made possible the improvement in the method. No essentially new feature is involved



in the new plug, but only the refinements of smaller and more accurate construction. The individual terminals are like those shown in Figure 2. As experience has been gained, it has become possible to dispense with various artifices formerly thought necessary, such as the secondary plastic packing above the cones, and the preliminary application of pressure with a heavy oil. At the same time the life of the insulation has been very much extended; seventy-five applications of 25,000 to 30,000 have been made before it was necessary to renew the insulation, whereas when this work started a single application could not be counted on.

In addition to this major improvement a number of minor improvements were made. The sensitivity of the grid with which the force driving the pistons is measured was doubled by changing the dimensions, making the grid shorter and thinner in section. The sensitiveness of the force measurement is now about one part in 200 at the maximum. This measurement was the mean of three settings on the potentiometer wire, with different directions of current flow and in a time sequence to eliminate effects due to any drift in the parasitics, and could be counted on to the limit of sensitivity of the individual readings, 0.1 mm. on the slide wire, or perhaps a trifle better. The sensitivity of reading of piston displacement was, with the original arrangements, some ten or twenty times as great as this. So great sensitivity could not all be used, and therefore opportunity was taken to improve the design of the piezometer and pistons, at the same time cutting down the displacements to one half. This was done by giving the piezometer the design shown in Figure 1 and in greater detail in Figure 3. The effective occupied length, that is, the length of the charge, is cut to one half by enlarging the mouth of the piezometer at both ends as shown. The stroke of the piston is correspondingly cut in half, which makes it possible to more effectively support the piston and minimize its plastic flow and lateral expansion. The new design of the piezometer decreases the friction of the charge as it slides on the sides of the piezometer by more than a factor of two, friction being exponential in the length, increases the bursting pressure of the piezometer appreciably because of the support afforded by the end regions

FIGURE 1. General view of the assembly, showing how the motion of the pistons of the piezometer (upper part) is transmitted to the measuring wire (lower part).

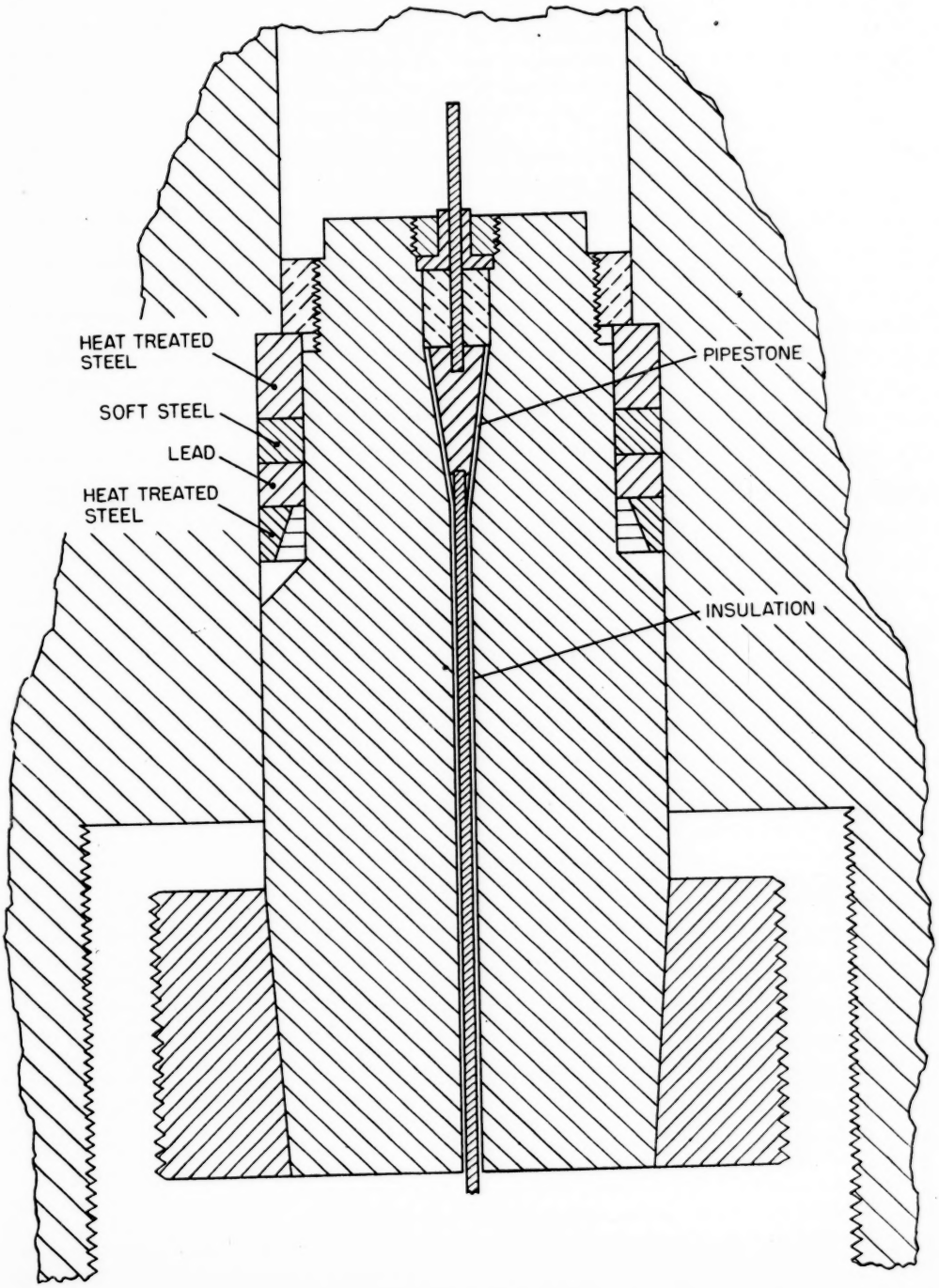


FIGURE 2. Improved design for getting electrical leads into the pressure cylinder, together with the improved split ring packing.

which are not exposed to internal pressure, and by the same mechanism decreases the barreling of the interior under internal pressure and so minimizes a small source of error in the computed distortion of the piezometer. The piezometers were made of grade 799 carboloy, with shrunk on steel jacket. This grade of carboloy has proved exceedingly well adapted for this purpose, no piezometer made of this grade ever having ruptured in use. In my earlier work ruptures of the

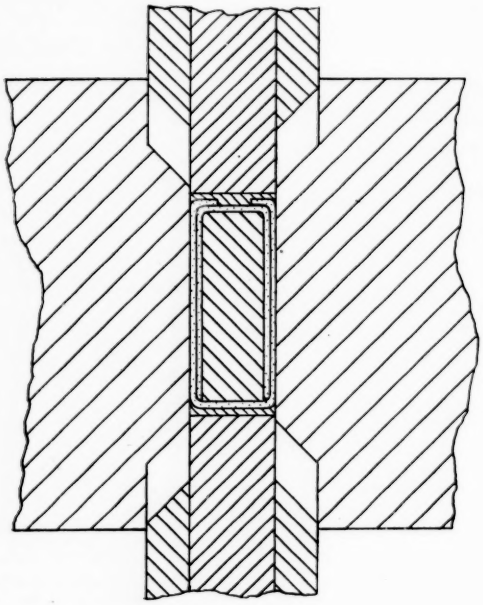


FIGURE 3. Enlarged view of the piezometer, showing method of sealing an alkali metal inside a double capsule of aluminum.

piezometer were common, but the piezometers were then made of the less suitable 905 grade. In the present work one piezometer has been exposed to 40 and the other to 50 applications of the maximum pressure, which was always at least as high as 100,000 and might infrequently reach nearly 110,000. The plastic flow of the piezometers under these conditions was slight. In use there is perceptible plastic enlarging of the interior, but this is very slow. During operation it was necessary to refigure only once by enlarging the bore from 0.0620 to 0.0625 inches. The pistons, as described previously, were best made of grade carboloy 999. The quality of this grade is not entirely uniform and it is desirable to make preliminary examination to find a batch with a high plastic flow point. In use the pistons are made 0.0004 inches smaller than the hole so that at no time will they expand sufficiently to touch the sides of the cylinder and thereby introduce friction. Under these conditions the pistons permanently expand by about 0.0001 inch after every excursion to the maximum, and they have to be refigured after every such use. Eventually after perhaps a dozen or fifteen refigurings the flow limit is reached, minute cracks begin to appear, and the pistons must be replaced. The shrunk on steel support around the unused part of the piston, as shown in Figure 3, materially adds to the life; there is no plastic flow in this part of the piston. The clearance of 0.0002 inches between piston and cylinder walls is large enough to put demands on the cup shaped steel packing between the end of the piston and the charge. If this is made of a soft steel it will be extruded between piston and wall with consequent friction and also danger of discing off the end face of the piston where it is pinched. A packing made of a heat treated steel with a Rockwell C hardness of 40 gave no trouble from this extrusion.

Friction between charge and cylinder walls was further materially reduced below that attained by halving the length of the charge by completely encasing the charge in an indium sheath. This sheath was formed in place in the cylinder with a suitable forming tool. There is, of course, a disadvantage in that the presence of the indium cuts down the amount of working substance and furthermore introduces an additional correction because of its compression. The advantages, however, usually outweighed the disadvantages. If the substance is mechanically soft, such as aluminum or magnesium, the sheath may be omitted. The volume of the indium in the sheath was usually approximately one half that of the working charge. Quantities of indium and charge were determined by weighing in a specially constructed micro-balance good to better than 0.00001 gm.; the usual weight of the indium was around 0.016 gm.

Two improvements were made in the technique of handling the production of the supporting pressure of 30,000 kg/cm^2. At one time a long series of capricious irregularities was encountered which was finally traced to freezing of the transmitting liquid, i-pentane. This was commercial material from the Eastman Kodak Company. The trouble was finally associated with the use of a new batch of this liquid. The explanation is

that Eastman has recently improved their method of preparing this liquid, so that it is now purer than formerly and therefore has a sharper freezing point. The remedy is to mix with the i-pentane half its volume of commercial "pentane." Even this mixture at the maximum pressure capriciously becomes sufficiently viscous to introduce appreciable non-hydrostatic forces, so that a redesign of the method of coupling the pistons to the slide wire measuring their displacement was necessary. Originally the coupling was by push contact for one direction of stroke, but on the reverse stroke a stiff spring was used to maintain contact. The spring was not strong enough always to overcome the stiffness of the liquid, so that the connection had to be redesigned to ensure positive transmission of motion for both directions of stroke. The second change in technique was in the packing ring closing the insulating plug at the bottom of the 30,000 apparatus. This had never been entirely satisfactory, but would leak slightly after long use in a way not easy to definitely locate. It appeared that after prolonged use with consequent work hardening the packing ring becomes loose on the inside surface, while remaining tight at the outside. The remedy was to make the packing ring double, an inside part sliding conically in the outer part, as indicated in Figure 2. In virtue of slip on the conical surface the inside as well as the outside now is pressed tightly against the retaining walls. Some fifty applications have been made without leak, the apparatus then having been taken down for another reason.

The various corrections and calibrations necessary in connection with the slide wire method of measuring displacement were determined by methods sufficiently obvious which have been previously used, so that they need not be described again in detail. It is an advantage of the method that the corrections are all small. The pressure coefficient of resistance of the wire was determined by a pressure run with the wire clamped. The validity of the corrections and calibrations was checked by measuring between 25,000 and 30,000 a known displacement of the same magnitude as the piston displacements encountered during the compression measurements. This was done by measuring the plastic shortening of a cylinder of copper, the shortening being terminated by a hardened steel stop when it had progressed by a known amount. The driving force is plotted as a function of displacement. There is a discontinuous change in direction when contact is first made with the copper and again when the stop is encountered. Since the cubic compressions of steel and copper are known, all the material is at hand for a calculation of the expected displacement, thus permitting a comparison with that given by the slider. The two measurements differed by 0.0001 inch on a displacement of 0.0350 inch, which is agreement to better than the sensitiveness of the force measurements.

The new set-up permits a check of a correction in the measurement of driving force by means of the grid. This correction is for the pressure coefficient of the simple compression coefficient of the electrical resistance of the grid. It is the largest of any of the corrections in this work, rising to something over twenty per cent. It had been previously determined from the average of several hundred determinations of the extra force required to drive the main piston of the 30,000 apparatus when it makes up against the grid. There is a rather large component of friction, and there was much scatter in the individual readings, so that an entirely independent confirmation was desirable. The possibility of such confirmation was afforded by the method used for studying the effect of pressure on the tensile strength of brittle substances described in a previous paper (2). The tension specimen is replaced by a double specimen of hardened steel, as indicated in Figure 4. A thin copper sheath unites the two steel pieces. The specimen was mounted in the holder for tensile specimens in the 30,000 apparatus, and, at a pressure of 21,000, the tensile force is measured which is required to separate the two steel specimens by measuring the change of resistance of the grid. The thin copper sheath prevents entrance of the transmitting liquid between the ends of the steel pieces, so that the force required to separate the steel pieces is equal to the force exerted by the known hydrostatic pressure over the cross section, plus a

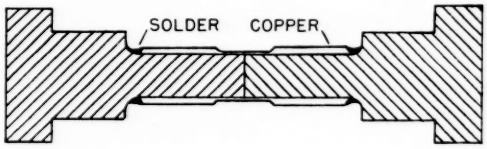


FIGURE 4. The compound tension specimen, with which the correction for the effect of pressure on the compressive constant of the "grid" is determined.

small correction, about 2 per cent, for the breaking strength of the copper. The agreement was perfect between the separating force determined from the hydrostatic pressure and that calculated from the resistance change of the grid using the previously determined pressure correction, thus checking the latter.

Having determined the displacements and the force on the piston, the final results are to be computed in exactly the same way as in previous papers, so that this need not be described again. In this computation the fiducial volume is that at 25,000 kg/cm². For many of the substances of this paper an independent determination of this has not been previously made, so that new measurements up to 25,000 were desirable. These were made in a new apparatus permitting very rapid measurements at room temperature with very small corrections. This apparatus has been previously described (3) and results obtained with it for 61 substances up to 25,000 kg/cm². It has now been found that the same apparatus can be used without modification up to 40,000 instead of 25,000 and measurements have been made with it on some 175 new substances, including those of this paper. For these substances we thus have overlapping measurements by two different methods in the range between 25,000 and 40,000, which affords a desirable check. This check, however, is not given under optimum conditions, since the comparison is between the upper end of the range of one instrument and the lower end of the range of the other. In a few cases the fiducial volume at 25,000 was not independently known from other experiments. In these cases it is possible to obtain a fairly satisfactory value from the absolute setting of the potentiometer when the high pressure pistons first establish contact with the grid in the neighborhood of 25,000. It is the differential settings of the potentiometer which determine the volume changes above 25,000.

The final results are, as before, strictly differential results between the substance in question and gold, assuming for the latter an extrapolation by Murnaghan's formula. Even if the accuracy of the measurements permitted it, which they do not, we are not yet in a position to obtain the absolute compressibility of any single one of the relatively incompressible substances up to 100,000 with any accuracy. The relative compressibilities, however, are determinable within the accuracy of the measurements.

In making the measurements, complete data were recorded for the piston displacement by both the former (external piston) and the new (slide wire) methods. The displacements by both methods were calculated for about half the substances. These definitely established the superiority of the new method, both in smoothness and consistency, while at the same time showing no over-all discrepancy between the two methods, so that there is no reason to fear any consistent error in the results already published. In view of this and also of the fact that calculations by the former method are much more time consuming than by the new, only the new data by the slider method were used in the computations for the other half of the substances.

As before, most of the substances were independently measured in two different piezometers. There are, however, a few of the more incompressible and unusual elements which have been measured in only one piezometer. Since in any event no high accuracy can be expected for these elements the chief interest of the measurements for them lies in the information obtained with regard to the presence or absence of new polymorphic forms in the new pressure range.

The detailed presentation of results now follows. The order is: first the five alkali metals in order of atomic weight, then 17 other elements in order of atomic weight, then ten compounds including the sulfides, selenides and tellurides of zinc, mercury and lead, and quartz crystal, and finally six glasses.

Detailed Results

Alkali Metals. Results for all of these metals except caesium have already been published. These are of especial theoretical interest because the structure of these elements is sufficiently simple to permit theoretical calculation of the volume changes under pressure. Furthermore, they should at first sight be among the easiest to measure experimentally because the compressibilities are among the highest of the elements. Unfortunately, however, they turn out to be among the most difficult to determine experimentally, and of all the materials formerly measured the results were least accurate for them. It was therefore thought to be worth while to redetermine them with the present more accurate method. The difficulty arises from the great mechanical softness of these metals and their high chemical activity. It had already been established that the carboloy piezometer is ruptured if pressure is directly transmitted to it by sodium,

and there was evidence that lithium might produce a similar fracture. Accordingly the alkali metal has to be enclosed in some sort of a protecting sheath. This sheath should obviously be as soft mechanically as feasible. In the previous work a sheath of copper was used, the total volume of the copper being of the order of twice that of the metal and its contribution to the compressibility of the order of one fifth that of the alkali. The friction exerted by so much copper proved to be sufficient to introduce a rather large uncertainty into the final result. In attacking the problem again, search was first made for a softer metal out of which to make the protecting sheath. Sodium was first tried in a sheath of indium. On application of 100,000 there was a large permanent change of volume, and on release the two metals were found to be completely alloyed. Sodium in a sheath of lead was then tried. Again there was an irreversible and permanent decrease of volume, much less than before, but too much. On cutting open the capsule a region of alloying was found at the surface of contact. It was concluded from this experience that alloying would be produced in the cold by these high pressures if the alloy existed. The extremely extensive book of M. Hansen on binary alloys of the metals was then consulted, and the softest metal known not to alloy with the alkali metals found to be aluminum. This is harder than would be desirable, but still much softer than copper. The aluminum sheath was made in the form of a double cup, as indicated in Figure 3. A simple technique was worked out by which the filling was accomplished under petroleum ether, the petroleum ether removed by evaporation, still leaving a protecting atmosphere of petroleum ether, the outer cup slipped over the filled inner cup, and the projecting edge of the outer cup swaged over the inner cup while still in the protecting atmosphere, and then the final closure of the cup accomplished by spinning in a jeweler's lathe. The atmosphere was thereby effectively excluded, and the capsules were capable of remaining indefinitely in the air of the room with no evidence of chemical action. The quantities were determined by an initial weighing of the aluminum cups and a final weighing of the filled capsule. In the case of caesium the room was cooled to about 10° C by opening the windows during the filling, and all pieces of metal in contact with any part of the filling apparatus as well as the petroleum ether were prechilled to 0° C. Caesium was not previously measured above 45,000. The reason for this was entirely accidental; the apparatus for 100,000 had been filled and pressure applied up to the maximum when the piezometer broke. This was at the end of the previous series of measurements, when war work was pressing to be done, and I was not able at that time to return to it. Except for the inconvenience of the low melting point, there is no greater intrinsic difficulty with caesium than with any of the other alkali metals, and the same arrangements will serve.

The source of the alkalies, except caesium, was my own stock, with which many of my previous results have been obtained and known to be of adequate purity, kept sealed under Nujol. The caesium, however, was obtained from a previously unopened glass capsule sealed in vacuum obtained from Mackay before the war, one of several such capsules, others of which had been used in my previous work. The caesium was obviously impure with its own oxide, as shown by its bright yellow color and indefinite freezing. It was purified, as in my previous work, by distillation at the minimum temperature in a high vacuum and over an interval of several hours. The evidence of purity is the disappearance of the yellow color and sharpness of freezing.

The volumes of the five alkalies obtained with the present apparatus are shown as a function of pressure in Table I. As already mentioned, the volumes at 25,000 kg/cm² are those given by measurements in the new apparatus for 40,000. Values of the volumes below 40,000 will be found in a paper following this describing the reults with that apparatus. It is debatable how best to present the final results in the pressure range in which there are independent determinations with different pieces of apparatus. In some of my early work the course was adopted of adjust-

TABLE I

VOLUME OF THE ALKALI METALS

Pressure kg/cm²	Lithium	Sodium	Potassium	Rubidium	Caesium
1	1.000	1.000	1.000	1.000	1.000
25,000	.851	.789	.691	.675	.609
30,000	.833	.770	.668	.652	.571
40,000	.801	.737	.628	.612	.521
50,000	.773	.708	.595	.578	.431 *
60,000	.748	.683	.568	.551	.409
70,000	.727	.661	.546	.528	.392
80,000	.707	.641	.528	.507	.381
90,000	.689	.623	.513	.489	.375
100,000	.672	.606	.500	.473	.368

* Discontinuity of volume of .056 at 45,000

ing the values given by one apparatus in the direction of those given by the other in the overlapping ranges. Such a procedure is obviously to a certain extent arbitrary. The simpler and perhaps safer course is now adopted of reporting the results obtained with the present apparatus for 100,000 without any adjustment at all for the results obtained with the 40,000 or other forms of apparatus. The values obtained with the two pieces of apparatus at 40,000 will be stated however. This will put the reader in a position, in conjunction with the data of the other paper, to make his own adjustments as he sees fit. The same course will be followed with the other materials of this paper. The comparison of the results with the two pieces of apparatus is as follows. At 40,000 the volume obtained with the 40,000 apparatus for lithium was 0.796 against 0.801 with the present 100,000 apparatus; for sodium 0.726 against 0.737; for potassium 0.633 against 0.628; for rubidium 0.605 against 0.612; and for caesium 0.518 against 0.521. The results with the 40,000 apparatus at 40,000 are somewhat lower than with the present apparatus, which means that the 40,000 apparatus gives a somewhat greater compressibility in the range 25,000 to 40,000 than does the present apparatus.

Compared with the previous measurements to 100,000 the new measurements give consistently larger volumes at the top pressure than before. The difference is spread over the entire pressure range, but accelerates markedly at the upper end of the range. The comparison of the volumes at 100,000 is as follows: for lithium 0.672 now against 0.606 before; for sodium 0.606 against 0.560; for potassium 0.500 against 0.427; and for rubidium 0.473 against 0.362. The new results give a more rapid falling off of compressibility at the high end of the range than formerly, which is in the direction which certain theoretical considerations had suggested as probable.

By far the most interesting of the new results is the volume discontinuity found for caesium at approximately 45,000, just at the end of the previous measurements. The single run previously made with increasing pressure just before the apparatus broke showed the same effect. The volume change is comparatively large, about 11 per cent. This volume change is in addition to the one already known at about 23,500 kg/cm^2 (5), at which occurs a change from the body centered to presumably the face centered arrangement, according to the calculations of Bardeen (6). The new transition must therefore be from an arrangement which is already close packed to something else; the question is what can it be. The new transition is clean cut, reversible, and runs rapidly in either direction with little pressure transgression. Above the transition the new modification of caesium has, in comparison with the other alkalies, an unexpectedly small compressibility, which drops off abnormally rapidly with increasing pressure. In the table a reversal in the trend of the compressibility to drop with increasing pressure is indicated at the last interval between 90,000 and 100,000. This may or may not be real; the figures were given as they came without final smoothing.

Other Elements. In Table II the volumes of 17 other elements are given up to 100,000. In general those elements were chosen which had not already been measured which have a compressibility large enough to be inviting. A five per cent change of volume at the maximum pressure is about the minimum that should be attempted—ten per cent is better. In addition to these a number of elements were tried whose position in the periodic table suggested them as candidates for polymorphic transitions.

Detailed comment on the elements of Table II now follows.

Beryllium. The material I owe to Professor John Chipman of M. I. T. The purity is said to have been about 99.7 to 99.8 per cent with possible inclusion of oxygen. It was from the same batch as a specimen whose tensile behavior under pressure has been reported elsewhere (7). Beryllium is the most incompressible of the elements examined here. Acceptance of the data at their face value would indicate a compressibility increasing with pressure. This was not borne out, however, by the independent measurements in the 40,000 apparatus. The best course is to assume a linear relation between pressure and volume between 25,000 and 100,000. The table does not list the intermediate volumes in order to give no false impression about the accuracy. The most important result is that there is no marked transition below 100,000.

Carbon (graphite). The material was single crystal Ceylon graphite in sheets of the order of .005 inches thick which I owe to the courtesy of Sir K. S. Krishnan a number of years ago. It was cut into discs with a tubular cutter. The discs were then stacked and assembled in the indium sheath. Measurements have been previously made and published on the same material to 25,000 (8); measurements were not now re-

TABLE II

VOLUME OF VARIOUS ELEMENTS

Pressure kg/cm²	Be	C (Graphite)	Mg	Al	Si	Phosphorus Black	Phosphorus Violet	Ti	Mn	Ge	As	Zr	La	Ce	Pr	Nd	Th	U
1	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
25,000	.978	.947	.943	.970	.978	.935	.903	.978	.961	.968	.955	.974	.917	.797	.927	.935	.962	.978
30,000		.940	.935	.966	.974	.927	.885		.956	.964	.947	.967	.904	.788	.916	.925	.952	.973
40,000		.929	.919	.958	.968	.912	.853		.947	.956	.933	.956	.882	.770	.896	.906	.937	.966
50,000		.919	.904	.951	.962	†{.899 .849	.829		.939	.949	.921	.946	.863	.756	.878	.889	.924	.960
60,000		.911	.890	.944	.957	.837	.809		.932	.942	.911	.937	.846	.744	.863	.873	.913	.955
70,000		.903	.878	.937	.952	.825	.793		.926	.935	.903	.929	.832	.732	.849	.858	.904	.951
80,000		.896	.866	.929	.948	.816	.780*		.922	.929	.896	.922	.819	.722	.836	.845	.897	.947
90,000		.890	.856	.922	.944	.807	.667		.918	.923	.890	.916	.808	.714	.823	.833	.891	.944
100,000	.945	.885	.847	.915	.940	.799	.660	.937	.915	.917	.884	.910	.798	.708	.811	.822	.886	.941

No transition

† Reversible transition

* Irreversible transition at 85,000 from violet to black. Volumes: 0.773 and 0.670

peated in the 40,000 apparatus. The results should be fairly good, because the slope of the curve obtained with the 25,000 apparatus fits on smoothly with the results now found.

Magnesium. This was from stock obtained a number of years ago from the Research Laboratory of the Aluminum Company of America and had been especially purified. It was used directly, without the intervention of an indium sheath, the mechanical softness being sufficient. The results therefore do not depend on any corrections for the effect of the sheath. The compressibility has been previously measured (9) only to 12,000 kg/cm². The fiducial volume at 25,000 was assumed to be 0.943 by extrapolation of the former results according to the formula:

$$-\Delta V/V_\circ = 29.50 \times 10^{-7}\, p - 26.7 \times 10^{-12}\, p^2.$$

The slope at 25,000 of the new results agrees as well as could be expected with the extrapolated slope, being 0.017 against 0.016.

Aluminum. The material was cut from a Bureau of Standards melting point sample. Four runs were made: two with an indium sheath and two without. The agreement between the two sets was not as good as desirable, the volume at 100,000 given by the former being 0.903 against 0.915 by the latter. The latter was made the basis of the results in the table, since it is presumptively more correct because of the absence of correction for the sheath. The variation of compressibility given by this series, however, is presumptively not correct, a slight increase of compressibility with increasing pressure being indicated, in opposition to the definitely indicated decrease of compressibility of the much more accurate measurements by the method of linear compressibility, as yet unpublished, to 30,000. The course was therefore adopted of showing a linear decrease of volume in the table between 25,000 and 100,000.

Silicon. This material I owe to the kindness of Dr. W. Shockley of the Bell Telephone Laboratories; it had been highly purified. There are no previous measurements of the volume to high pressures. The fiducial volume at 25,000 was calculated from the absolute potentiometer setting at contact. This value lies smoothly enough between the atmospheric volume and the values at higher pressures. The only previous determination of the compressibility of silicon appears to have been by T. W. Richards (10) over a pressure range of 500 kg/cm²; his value was 3.1×10^{-7}. This is much lower than the value indicated by

this new work. The early specimens of silicon were notoriously impure, and inadequate impurity is doubtless the major source of the discrepancy.

Phosphorus. 1. *Black phosphorus.* This was from my old stock, made from yellow phosphorus ar 12,000 kg/cm² and 200° C. some 20 years ago. There are no other measurements of the volume at high pressures. The fiducial volume at 25,000 necessary in the present calculations was taken from the absolute potentiometer setting. Black phosphorus has a transition with comparatively large change of volume which runs with increasing pressure at 55,000 or 60,000. The reverse transition, however, with decreasing pressure does not run above 25,000, and therefore was not observable with the present set-up. The fact that it does run, and that the transition is therefore of the thermodynamically reversible type, was established in two ways: by the return of volume to normal value at atmospheric pressure and subsequent repetition of the entire pressure cycle when the measurements were repeated on the same sample in the second piezometer, and by X-ray determinations of the structure of the material after exposure to 100,000. The X-ray examination was most kindly made by Professor B. F. Warren of M. I. T., who found the same normal black phosphorus structure which he had previously determined. In the table the transition pressure is indicated as 50,000; this can be only rough. It is probably much closer to the lowest pressure at which the transformation runs spontaneously with increasing pressure than to the pressure of thermodynamic equilibrium. Naturally the volumes indicated in the table for the low pressure phase had to be obtained from the readings with increasing pressure only, instead of being an average of increasing and decreasing as usual.

2. *Violet phosphorus.* This also was from my old stock, formed at about the same time as the black phosphorus and described in previous publications (11). Only one run was made with this, and the volumes in the table are obtained from the readings with increasing pressure only. This was necessary because between 80,000 and 90,000 the violet is transformed irreversibly to black, as is indicated in the table. The identity of the transformation product was again most kindly established by Professor Warren by X-ray analysis, who found the conventional black phosphorus lines, but much broadened, indicating a fine grained and distorted structure, as would be expected from the manner of formation. Professor Warren also made an X-ray examination of the original violet phosphorus and found a line pattern somewhat better developed than the line pattern of many other varieties of red phosphorus. Up to the present, however, he has not been able to index the pattern of either this or any of the other varieties so that for the present the exact identity of this material is not known.

The markedly greater compressibility of violet phosphorus in comparison with black is to be noted. This is in the direction to be anticipated. The transformation of violet to black phosphorus has already been accomplished at a pressure of 40,000 kg/cm² combined with plastic flow in shear (12). The transformation found in this paper is the first time that it has been accomplished by pure hydrostatic pressure. The great efficacy of shearing stress in promoting a transition which is thermodynamically possible but which is resisted by internal viscocity is apparent.

Titanium. This was from a lot recently obtained from A. D. Mackay, said to be of 99 per cent purity. It was hard and brittle, and was one of the most incompressible of the substances measured here. As in the case of beryllium, the measurements taken at their face value indicate a compressibility which is least at the lower end of the range, increasing somewhat to a roughly constant value at pressures over 50,000. This is not in line with the results obtained with the 40,000 apparatus, which indicated a normal decrease of compressibility with rising pressure up to 40,000. The best that can be done with the present results is to assume a linear relation between volume and pressure up to 100,000, and to take the volume actually obtained at 100,000 as giving the best mean compressibility. The most important result is that there is no large transition. Only a single piezometer was used.

Manganese. This material was obtained through the kind offices of Dr. B. A. Rogers before the war from the U. S. Bureau of Mines in Salt Lake City. The analysis given was 1.02% Ni, 2.33% Cu, 0.1% Si, balance Mn. The compressibility was not measured in the 40,000 apparatus; the fiducial volume at 25,000 was obtained from the absolute potentiometer setting. The compressibility thereby indicated for the low pressure end of the range fits on smoothly with that obtained with the present apparatus above 25,000. In view of the complicated crystal structure of manganese it might perhaps have been anticipated that it would exhibit transitions.

Perhaps the comparatively large amount of copper may have suppressed such a transition.

Germanium. This I owe to the kindness of Professor Lark-Horovitz. It had been used by him in his low temperature investigations of the Hall effect and was of his "N" type. This was measured also in the 40,000 apparatus; the volume at 40,000 obtained with it was 0.952 against 0.956 above.

Arsenic. This was from my single crystal stock, the same as that used in previous measurements (13), and known to be of high purity. The effect of pressure on this substance is known to be complicated; measurements of the linear compressibility to 12,000 kg/cm² indicated great differences in different directions and a condition of not well defined internal equilibrium. The volume compression has been measured to 25,000 and the fiducial volume at 25,000 was taken from those measurements (3)—no measurements were made with the same apparatus to the new range of 40,000. The present results do not join on quite smoothly with the former ones to 25,000, the new ones giving a higher compressibility at the low end of the range. The former results gave a volume decrement between 20,000 and 25,000 of 0.0062, and the new results between 25,000 and 30,000 of 0.075. There was no perceptible permanent change of volume after the first application of 100,000.

Zirconium. This was from the same specimen as that previously measured (14) to 12,000. It was obtained from the laboratory of the Philips Lamp Works in Eindhoven, was soft and malleable and presumably of high purity. Measurements to 100,000 were made in only a single piezometer. The fiducial volume at 25,000 was obtained from measurements with the 40,000 apparatus. This gave for the volume at 40,000 0.960 against 0.956 above. No transition was found; the compressibility drops smoothly with increasing pressure.

Lanthanum. This was obtained from Mackay, without statement of the probable purity. It was shipped under oil to avoid oxidation, was soft, and had every appearance of sound, homogeneous, pure metal. This was the first measured of four rare earth metals in consecutive places in the periodic table, namely La, Ce, Pr, and Nd. Very little work has been done on these previously under pressure. Cerium, however, is known (15) to be anomalous, having a rather large transition near 7,000 and the low pressure phase, being one of the few substances with a compressibility increasing with increasing pressure. It suggested itself that the other rare earth metals might also show abnormalities; the only one found was a transition of lanthanum with .0026 volume change at 23,400 kg/cm².

Measurements were made on lanthanum to 100,000 in only a single piezometer. It was also measured in the 40,000 apparatus and the fiducial volume at 25,000 obtained from those measurements. Since lanthanum is among the more compressible of the substances measured here the results may be accepted with some confidence. The volume at 40,000 given by the 40,000 apparatus was 0.881 against 0.882 above.

Cerium. This was obtained from Mackay at the same time as the lanthanum and the same remarks apply to it. Measurements in the 40,000 apparatus gave for the volume at 40,000 0.766 against 0.770 above. It will be seen that no new anomalies were found above the transition, and the compressibility of the high pressure phase decreases normally with increasing pressure. The data to 40,000 should be consulted; they differ materially at low pressures from the previous data.

Praseodymium. This was obtained from Mackay and the same remarks apply as to lanthanum and cerium. Measurements were made in both the 40,000 and the 100,000 apparatus; for the latter only a single piezometer was used. No anomalies were found, at either high or low pressures. The volume at 40,000 given by the 40,000 apparatus was 0.893 against 0.896 with the 100,000 apparatus.

Neodymium. This was also obtained from Mackay, and the same remarks apply as to the three other rare earth metals. Measurements to 100,000 were made in only a single piezometer. The volume obtained with the 40,000 apparatus at 40,000 was 0.905 against 0.906. No anomalies were found in any part of the range.

Thorium. This was also obtained from Mackay. It was in the form of rolled sheet, 0.004 inches thick. The purity was not stated. It was punched into discs, which were stacked for the measurements to 100,000, using an indium sheath as usual. Only a single piezometer was used to 100,000 and no measurements were made with the 40,000 apparatus. No anomalies were found in the high pressure range. The compressibility of thorium has been previously measured (16) to 12,000 for which the formula was found:

$$\Delta V/V_\circ = -\ 18.15 \times 10^{-7}\, p + 11.22 \times 10^{-12}\, p^2.$$

The fiducial volume at 25,000, 0.962, was obtained by extrapolation from this formula. At 50,000 the same formula gives 0.912 against 0.924 found above.

Uranium. This was old stock of unknown origin which I had had for a number of years. It is one of the more incompressible of the elements measured here, so that the results are relatively less reliable. The behavior found was normal in every respect. Uranium is mechanically much softer than either beryllium or titanium, and no indication of an anomalous increase of compressibility was found. The fiducial volume at 25,000 was obtained from the 40,000 apparatus, which gave for the volume at 40,000 0.9676 against 0.966 above.

Certain Compounds. In Table III the volumes of nine compounds are given: the sulfides, selenides and tellurides of zinc, mercury and lead. These have already been measured (17) to 50,000; the material used in the new measurements is the same as that of the old.

TABLE III

VOLUME OF VARIOUS COMPOUNDS

Pressure kg/cm²	ZnS	ZnSe	ZnTe	HgS	HgSe	HgTe	PbS	PbSe	PbTe
1	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
25,000	.972	.955	.950	.922	.853	.870	.933	.938	.944
30,000	.968	.950*	.944	.920	.844	.863	.928	.932	.939
40,000	.961	.940*	.933*	.916	.829	.847	.918	.922	.930
50,000	.954	.930	.922	.912	.816	.832	.909	.888*	.884*
60,000	.947	.921	.911	.906	.805	.817	.900	.877	.869
70,000	.940	.912	.899	.899	.795	.803	.892	.867	.855
80,000	.934	.904	.888	.892	.788	.790	.886	.858	.842
90,000	.929	.895	.878	.885	.782	.777	.881	.849	.831
100,000	.924	.887	.868	.879	.777	.765	.876	.841	.820

* Small transition at 38,000

* Small transition here

* Transition at 45,000. Vols. 0.917 and 0.893

* Transition at 45,000. Vols. 0 925 and 0.892

ZnS was measured in the form of sphalerite; the form wurtzite is known to be changed by pressure and shear irreversibly to sphalerite (18). Nothing notable was found in the new range. At 50,000 the volume was formerly found to be 0.951, to be compared with 0.954 found now.

ZnSe was formerly found to have a transition in the neighborhood of 38,000 kg/cm² with volume discontinuity of .004. This is too small to be definitely indicated in the present results, which were smoothed right over the transition. The volume at 50,000 given by the previous measurements was 0.931 against 0.930 now.

The former measurements on ZnTe gave a transition with volume discontinuity of 0.005 in the neighborhood of 40,000. This transition was perceptible in the readings with increasing pressure with one of the piezometers, but not with the other, which was more irregular than usual. The results in Table III are accordingly smoothed over the transition. At 50,000 the former value of the volume was 0.907 against 0.922 given now. The difference is greater than usual and is doubtless connected with smoothing over the transition.

The measurements with HgS were not as satisfactory as desirable. The material was the red sulfide, previously used to 50,000. The first run to 100,000 gave an abnormally high compression up to 80,000, and then a further volume discontinuity indicating a transition. Unfortunately the slider stuck because of viscosity in the transmitting medium (this was before this defect in the apparatus had been corrected) with decreasing pressure, and the results of the run were discarded. The run with the second piezometer gave perfectly satisfactory readings on the identical specimen, except that the compression was markedly less. One would suspect a permanent change of form after the first application, except that recovery of the initial volume at atmospheric pressure had been perfect. The present measurements indicate an increase of compressibility with pressure at the low end; it is questionable how much of this is real. The volume found in the former measurements at 50,000 was 0.892 against 0.912 found now. The difference is larger than usual and again indicates some unusual occurrence; X-ray analysis of the final product would be desirable.

The HgSe was material which had previously been exposed to 50,000. It is known to have a large transition near 7,500, which naturally did

not figure in the present work. The volume previously found at 50,000 was 0.820 against 0.816 found now. The high pressure measurements seem conventional enough; the decrease of compressibility with increasing pressure is perhaps somewhat greater than normal.

The HgTe was from the same batch of synthetic material as that formerly used, but this particular piece had not been formerly exposed to pressure. It was previously found that HgTe decomposes slowly under pressure to the elements. This decomposition prevented former measurements of the compressibility, but did not prevent the establishment of a reversible transition near 12,000 with 8.4 per cent volume change, slightly less than the change of HgSe. In this new work the decomposition was not encountered, doubtless because the volume was so much smaller and the application of pressure so much more rapid, 20,000 in the preliminary application being reached in two or three minutes. As a consequence of this there are no low pressure compressibilities which could be used by extrapolation nor any direct measurements to give the fiducial volume at 25,000. The value used in the table, 0.870, is a guess based on the known volume of HgSe and the known volume discontinuities at the transitions. The high pressure measurements appear normal enough. The compressibility at high pressures drops off with increasing pressure much less than it does for HgSe, and the volume curves cross.

The PbS was a piece which had been previously exposed to 50,000. It is known that there is a transition just below 25,000, which naturally did not appear in this work except as it enters the fiducial volume at 25,000, which was taken from the former measurements. The volume at 50,000 given by the former measurements was 0.901 against 0.909 found now.

PbSe has been previously found to have a polymorphic transition at 43,000 with volume discontinuity of 0.016. The transition was found with these new measurements with a somewhat larger volume change, 0.024. The new value is doubtless to be preferred, since the transition point is so near the end of the former pressure range that the transition may not have run to completion. The volume at 50,000 given by the previous measurements was 0.882 against 0.888 found now. Above the transition the compressibility falls off normally with increasing pressure. The compressibility of the high pressure phase is not markedly different from that which would be extrapolated from the low pressure phase.

The PbTe had not been used in the former measurements to 50,000 but had been seasoned by an application of 30,000. Again, as in the case of PbSe, the previous measurements showed a transition at about 42,000. The volume change found was 0.009. The transition was found in the present work, but with a much larger volume change, 0.033. Doubtless the former low value is to be explained by incomplete running of the transition. The volume previously found at 50,000 was 0.900 against 0.884 found now. The difference can be almost entirely explained by former incomplete running of the transition.

Quartz Crystal and Six Glasses. One point of interest in measuring the glasses was to find whether the abnormal increase of compressibility with increasing pressure found at low pressures persists at high pressures. In the case of quartz glass it had already been found (19) that there is a reversal near 35,000. The interest in measuring quartz crystal was to compare it with the glass. The three glasses "A", "C", and "D" in the following were from the same stock as that used in previous measurements (20) of the effect of pressure on rigidity. The glass was originally obtained from Dr. J. T. Littleton of the Research Laboratory of the Corning Glass Works. "A" was a potash lead silicate of very high lead content, "C" was a soda potash lime silicate, and "D" a soda zinc borosilicate. The quartz glass was from ordinary laboratory stock, selected to be free from visible imperfections. The quartz crystal was provided by Professor Birch, who had it worked to the special shape required for measurement in the 40,000 apparatus. After the measurements to 40,000 I cut from the specimen a smaller piece for measurement to 100,000. The borax glass was also provided by Professor Birch, from the same stock as that used by Dane and Birch in their measurements of the effect of pressure on viscosity (21).

The volume at 40,000 for quartz crystal found with the 40,000 apparatus was 0.921, against 0.926 given by the 100,000 measurements. The cubic compressibility of quartz crystal is also obtainable from previous measurements (22) of the linear compressibilities in different directions up to 12,000. The formula, corrected for my improved compressibility of iron, is:

$$\Delta V/V_\circ = -\ 26.45 \times 10^{-7} p + 22.6 \times 10^{-12} p^2.$$

This formula gives by extrapolation for the

TABLE IV

VOLUME OF QUARTZ CRYSTAL AND SIX GLASSES

Pressure kg/cm²	Quartz Crystal	Quartz Glass	Glass "A"	Pyrex Glass	Glass "C"	Glass "D"	Borax Glass
1	1.000	1.000	1.000	1.000	1.000	1.000	1.000
25,000	0.946	.923	.934	.921	.945	.932	.877
30,000	.939	.909	.923	.907	.936	.924	.866
40,000	.926	.885	.905	.885	.920	.909	.845
50,000	.914	.864	.890	.867	.905	.894	.825
60,000	.902	.847	.875	.851	.891	.880	.808
70,000	.892	.832	.862	.838	.878	.867	.792
80,000	.883	.819	.849	.827	.866	.855	.778
90,000	.875	.808	.838	.817	.854	.844	.765
100,000	.868	.798	.828	.809	.842	.834	.753

volumes at 25,000, 30,000, and 40,000: 0.948, 0.942, and 0.930 respectively. The agreement with the values of Table IV is as close as could be expected for an extrapolation of this magnitude.

Quartz glass, measured in the 40,000 apparatus, gave for the volume at 40,000 0.881 against 0.885 in Table IV. Measurements have also been previously made to 50,000. The previous volumes at 25,000, 30,000, 40,000, and 50,000 respectively were 0.928, 0.912, 0.884, and 0.861. Both the previous measurements to 50,000 and the new ones to 40,000 show well the reversal in $\left(\frac{\partial^2 v}{\partial p^2}\right)_\tau$ near 35,000. The measurements in Table IV to 100,000 do not show this so well, however, the point of reversal being too near the lower end of the range. It will be noticed that the compressibility of the glass drops off with increasing pressure, in the range above 40,000 where it has become normal, more rapidly than that of the crystal. This is to be expected.

The volume of glass "A" given by measurements in the 40,000 apparatus was 0.904 at 40,000 against 0.905 found now. The 40,000 measurements indicate a break in direction near 20,000, the glass being more compressible above this pressure than would have been extrapolated from the volumes at lower pressure. This behavior is not suggested by anything in the present range, the compressibility dropping off smoothly with increasing pressure.

Pyrex glass has been found previously to have the same abnormal increase of compressibility with pressure as exhibited by quartz glass. Previous measurements had not extended above 12,000. New measurements on pyrex up to 40,000 show that the anomaly vanishes in the neighborhood of 25,000. The volume at 40,000 found with the 40,000 apparatus was 0.887 against 0.885 of Table IV above. In the range of Table IV compressibility drops normally with increasing pressure.

Glass "C" measured in the 40,000 apparatus shows the same sort of anomaly in the neighborhood of 20,000 as glass "A." The behavior appears to be normal in the range above 25,000 covered in Table IV. The volume at 40,000 found with the 40,000 apparatus was 0.917 against 0.920 found above.

Glass "D" measured in the 40,000 apparatus shows the same type of anomaly as "A" and "C," except that it is even more pronounced and occurs at a pressure somewhat below 20,000 instead of above it. The volume at 40,000 given by the 40,000 apparatus was 0.895 against 0.909 above. The discrepancy is by far the largest of any found in this paper. All the measurements appeared normally good, and the explanation does not suggest itself. If the anomaly just below 20,000 were associated with a transition, and if this were suppressed in the high pressure measurements, perhaps because of the rapidity with which pressure was increased, the discrepancy would be qualitatively explained. However, a transition of this sort in a glass would be something new.

Borax glass, measured in the 40,000 apparatus, showed no low pressure anomalies. The relation between volume and pressure is definitely not reproducible by a second degree expression in the pressure, the initial rate of drop of compressibility compared with that at higher pressures being too high. At 40,000 the volume given by the 40,000 apparatus was 0.835, against 0.845 above. The discrepancy is larger than usual, but so also is the absolute change of volume. Borax glass is the most compressible of the glasses measured here; quartz glass is next. The shape of the curves of volume against pressure is not the same for these two glasses; they draw together between 25,000 and 50,000, and from 50,000 on draw apart again by a small amount.

Discussion

Perhaps the most interesting question raised by an extension of volume measurements into a new field of high pressure is whether there is any indication of the atomic break-down to be expected at astronomical pressures. Ultimately, at high enough pressures, it has been shown by Jensen (23) and others that the perfect gas law will be followed, or volume will be inversely as the pressure. This means that ultimately log vol will be linear in log p, with a slope of unity. In Figure 5, $\log_{10}$ vol is plotted against $\log_{10} p$ for the five alkali metals of this paper, for lanthanum, the next most compressible metal of this paper, for borax glass, and for CsBr, one of the most compressible of the salts, the data for which have been determined in a previous paper (24). With one exception, the curves are all concave downward. If curvature continues in this direction, the volume will vanish at infinite pressure. Asymptotic approach to a finite volume at infinite pressure would obviously demand a reversal of curvature. Now all the early equations of state, before the possibility of atomic disintegration was visualized, demanded almost without exception a finite limiting volume at infinite pressure. These high pressure measurements are sufficient to show the definite inadequacy of this point of view. Further than this, the curves do not suggest any very definite conclusions. They are obviously still a long way from approaching the limiting slope of unity, and might equally well be headed for other limiting slopes, which would mean that ultimately the volume becomes proportional to some power of the pressure other than the first.

Especial significance should doubtless be attached to the curve for caesium. There are two breaks in this curve corresponding to the two polymorphic transitions. The lower transition at 23,000 has a small volume change and the course of the curve is hardly affected on passing through it. The higher transition at 45,000, however, is something quite different. The volume change is much larger, and the high pressure phase is drastically different, because for it log vol against log p is concave upward, the only example of it. This is the direction of curvature consistent with a finite volume at infinite pressure, and is not the sort of thing associated with the atomic breakdown contemplated by Jensen. A plausible inference would seem to be that there may be a large number of intermediate episodes on the way to complete atomic disintegration. It seems not unreasonable to expect that the pressure domain beginning at roughly 10^5 or 10^6 atmospheres may be a domain of as much detail and structure, at present entirely unsuspected by us and beyond present theoretical attack, as the complex atomic domain of ordinary experience.

The high pressure end of the curve for potassium shows indications of an approaching reversal of curvature like that of caesium. Experimental error, however, makes this more uncertain; the large effect for caesium would seem to be beyond possible experimental error.

The curves for borax glass and for caesium bromide cross; that of the latter runs roughly parallel with that of the metals. The crossing indicates an abnormally high compressibility in the borax glass at the low pressure end of the range. This is what might be expected in a glass, the initial effect of increasing pressure being to remove the "slack" between the molecules, as in a liquid.

Incidentally, any crossing of the volume curves is inconsistent with a universal one parameter relation between volume and pressure, of which the simple one constant equation of Murnaghan (25) is a recent example. Murnaghan's more complicated equations, with two or more disposable constants, would be required to represent all the present results.

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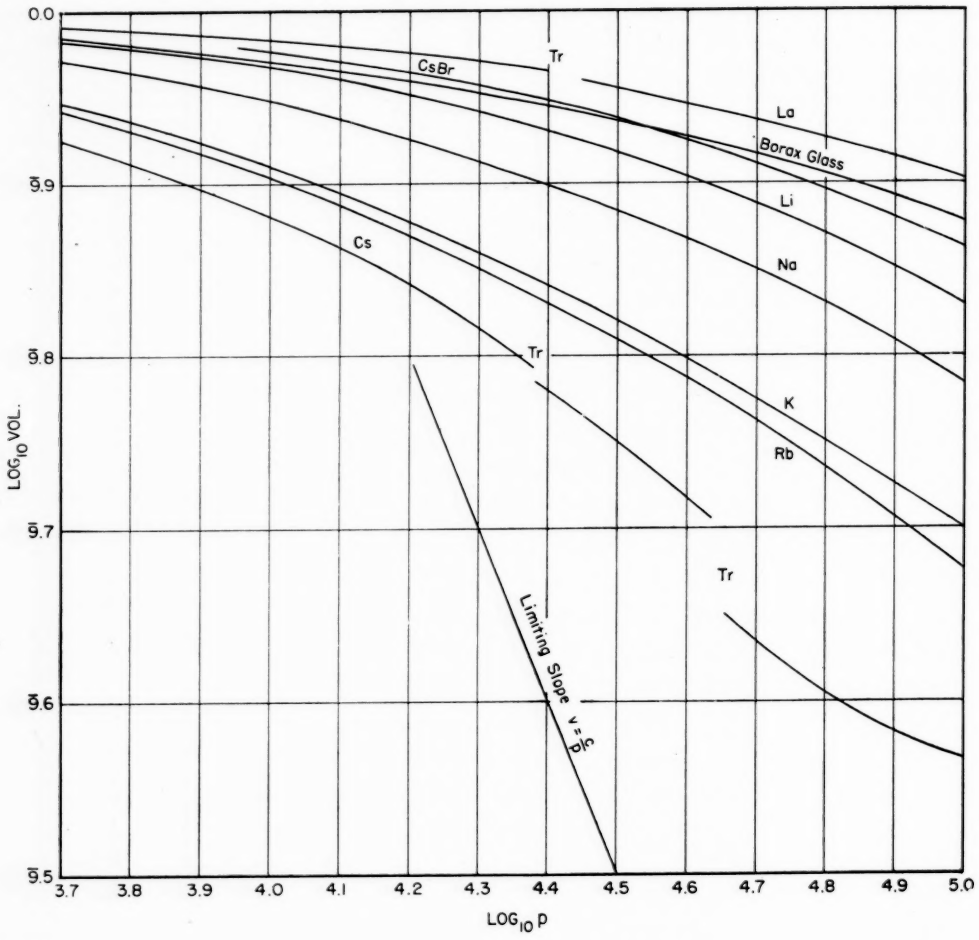

FIGURE 5. Logarithm of the volume against logarithm of the pressure up to 100,000 kg/cm² for a range of substances.

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ROUGH COMPRESSIONS OF 177 SUBSTANCES TO 40,000 KG/CM²

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Introduction

In a previous paper (1) an apparatus has been described for the rapid determination of the compression of solids at room temperature to high pressures, and the compression of 61 fairly compressible solids determined with it to 25,000 kg/cm². It was definitely not the intention to push this apparatus to the limit, but to use it as a tool of routine exploration in a range in which there would be no danger of fracture. It now appears that the limit formerly set was too conservative, for the same apparatus with minor modifications has now been carried regularly to 40,000, and the compression of 177 substances determined with it. Each substance involves two applications of maximum pressure, a preliminary "seasoning" application and the second stepwise application, up and down in steps of approximately 2,000 kg/cm², giving 43 readings in all. This has been accomplished with no fracture or measurable change of dimensions of the main pressure vessel. The short carboloy pistons, however, with which pressure is produced do not stand up indefinitely in this higher range, but have to be renewed from time to time. Failure of the piston is foreshadowed by the appearance of minute cracks, and since the piston can still be used several times after the first cracks appear, this has proved no disadvantage. One catastrophic failure occurred in the course of this new work. This was a failure of the steel column by which pressure is transmitted to the short carboloy piston, the column having been designed for the lower range of 25,000. Fortunately it was possible to redesign the column for the higher pressure range, and no further trouble has been encountered.

The materials investigated in the following have been selected as of interest from several points of view. The accuracy of the measurements naturally is greater for the more compressible substances, so that, in general, highly incompressible substances are to be avoided. Even these may be examined with profit, however, with regard to the possible existence of new polymorphic forms. There is no one guiding motif in the selection of the following material. The measurements have been made rather in the spirit of "scientific knitting," done in spare time between more systematic and important investigations. Since these measurements are mostly new, it has seemed worth while to at least record them.

The detailed presentation of data now follows, grouped into classes of substances.

Detailed Data

Plastics. Some 38 different plastics were measured, collected from a number of sources to have as wide a range of composition as possible. It was anticipated that there might be various transitions of higher orders among the plastics, that is, discontinuities in the various derivatives of volume, as a result of different stages of alignment of the long molecules. This did not turn out to be the case, however, but the curves were in almost all cases smooth.

The first six plastics shown in Table I were ordinary articles of commerce, taken from the laboratory stock. The Bakelite was clear amber stock, perhaps 25 years old. The "new" hard rubber was perhaps two or three years old, and the "old" about 25 years old. The purpose in trying rubber of two ages was to test whether there is any slow change with time. I owe to the courtesy of the du Pont Company the specimens of nylon and "Teflon" (polytetrafluorethylene), No. 29 in the table. The nylon 6–10 was cut from a sheet about 0.25 inch thick. The

TABLE 1

COMPRESSION OF VARIOUS PLASTICS

Pressure kg/cm²	Leucite	Polystyrene	Cellulose Acetate	Bakelite	Hard Rubber new	Hard Rubber old	Nylon 6–10	Nylon 6–6 unoriented	Nylon 6–6 oriented	α-Beetle Filler	Aeroglass 4121	Laminac 4201	Melmac 404	Melmac 1079	Melmac S–6004	48,000	41,000	46,000	2060–38
0	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000
2,500	.0367	.0409	.0468	.0240	.0316	.0360	.0385	.0331	.0380	.0241	.0437	.0350	.0226	.0237	.0182	.0313	.0279	.0347	.0370
5,000	.0671	.0724	.0784	.0438	.0610	.0642	.0655	.0594	.0665	.0439	.0712	.0599	.0421	.0434	.0331	.0545	.0510	.0619	.0656
10,000	.1097	.1200	.1189	.0760	.1045	.1068	.1060	.0961	.1061	.0757	.1136	.0967	.0741	.0754	.0567	.0894	.0853	.1028	.1098
15,000	.1387	.1519	.1486	.1022	.1345	.1372	.1348	.1233	.1340	.1000	.1427	.1245	.0992	.1004	.0753	.1148	.1119	.1324	.1417
20,000	.1611	.1756	.1717	.1235	.1573	.1600	.1570	.1444	.1559	.1202	.1658	.1469	.1199	.1208	.0906	.1359	.1337	.1554	.1656
25,000	.1796	.1946	.1905	.1413	.1760	.1785	.1749	.1617	.1739	.1371	.1841	.1650	.1368	.1376	.1035	.1535	.1520	.1742	.1846
30,000	.1949	.2104	.2065	.1564	.1917	.1938	.1900	.1768	.1893	.1512	.1996	.1803	.1509	.1516	.1149	.1686	.1671	.1900	.2004
35,000	.2078	.2240	.2200	.1695	.2050	.2070	.2029	.1899	.2024	.1632	.2127	.1935	.1632	.1636	.1248	.1810	.1803	.2031	.2138
40,000	.2184	.2359	.2318	.1812	.2166	.2188	.2139	.2016	.2136	.1739	.2241	.2052	.1737	.1738	.1334	.1916	.1919	.2146	.2252

TABLE 1—Continued

COMPRESSION OF VARIOUS PLASTICS

Pressure kg/cm²	M–1805	M–2348	M–1364	M–2347	M–2343	M–2345	M–2346	M–2344	M–2342	Teflon	Fluorine Plastic	Silicone 160	Silicone 181	Silicone 180	Silicone 167	Silicone 120	Silicone 125	Silicone 150	Silicone Glass filled
0	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000
2.500	.0553	.0548	.0522	.0435	.0383	.0424	.0399	.0435	.0474	.0527	.0398	.0835	.0746	.0653	.0669	.0814	.0872	.0737	0334
5,000	.0874	.0897	.0863	.0760	.0676	.0762	.0707	.0781	.0775	.0847	.0673	.1182	.1090	.0967	.1001	.1213	.1284	.1112	.0580
10,000	.1319	.1331	.1300	.1201	.1116	.4217	.1156	.1262	.1213	.1453*	.1037	.1580	.1529	.1368	.1385	.1676	.1734	.1522	.0930
15,000	.1621	.1639	.1606	.1504	.1440	.1526	.1467	.1569	.1525	.1694	.1282	.1796	.1788	.1595	.1580	.1901	.1974	.1757	.1177
20,000	.1852	.1876	.1836	.1733	.1685	.1763	.1698	.1797	.1766	.1875	.1474	.1951	.1995	.1779	.1729	.2081	.2153	.1941	.1378
25,000	.2040	.2066	.2024	.1917	.1880	.1952	.1883	.1979	.1960	.2019	.1628	.2081	.2176	.1937	.1852	.2229	.2303	.2091	.1551
30,000	.2194	.2222	.2178	.2074	.2042	.2108	.2038	.2130	.2118	.2143	.1755	.2194	.2336	.2076	.1960	.2351	.2429	.2220	.1703
35,000	.2321	.2351	.2306	.2206	.2178	.2234	.2167	.2262	.2250	.2248	.1862	.2297	.2475	.2197	.2055	.2455	.2531	.2330	.1835
40,000	.2430	.2460	.2416	.2315	.2293	.2336	.2275	.2375	.2362	.2339	.1956	.2390	.2592	.2303	.2139	.2545	.2614	.2424	.1955

*Transition at 6,500.
Vols, .1004 and .1230

nylon 6-6 was provided in a rod of approximately 0.5 inch diameter (unoriented). The "oriented" specimen of this 6-6 nylon was produced by upsetting a cylinder originally 1 inch long by one-sided compression between the platens of a hydraulic press until the thickness was reduced to 0.085 inch. It required about 45,000 psi to do this. Plastics 10 to 15 inclusive I owe to the courtesy of the American Cyanamid Company. Their description of them is as follows:

Melmac 404; Melamine-formaldehyde, no filler, at present an experimental product.

Melmac S-6004; Melamine-formaldehyde, asbestos filler.

Melmac 1079; Melamine-formaldehyde, alpha cellulose filler.

Beetle; Urea-formaldehyde, alpha cellulose filler.

Aeroglass 4121; Clear cast copolymer type, no filler.

Laminac 4201; Clear cast copolymer type resin similar to that used in laminating applications, no filler.

Plastics 16 to 28 inclusive I owe to the kind offices of Dr. C. O. Strother of the Linde Air Products Company, who obtained most of them from the Bakelite Corporation. The description is given in the appended table.

In addition to the plastics described in detail in the above table, four others obtained from Dr. Strother are described as follows. "Sample 206-38 is of the type known as a polyester resin. It is generally made by the reaction of a di-basic acid containing maleic acid with a glycol. This base resin is hardened with a vinyl material such as styrene. The samples marked 41000 and 48000 are phenolic formaldehyde types. Sample 46000 is a so-called glyptal. It is made by the reaction of a di-basic acid, such as phthalic, with glycerine or a like compound."

Plastic 30 is one of the experimental fluorine plastics developed during the war which I owe to the kindness of Dr. W. T. Miller of Cornell.

Plastics 31 to 38 inclusive are various silicone plastics which I owe to the courtesy of the Dow-Corning Research Laboratory. These silicones are described by the manufacturers as "Silastics," and various mechanical and electrical properties are given in their trade catalogue on silicones. Silastics 120 and 125 contain approximately 50 per cent by weight of titanium oxide and 50 per cent of high polymeric methyl silicone. Silastics 160, 167, 180 and 181 contain approximately 60

Designation	Formulation						Properties of Base Resin		
	Base Resin			Plasticizer (plus stabilizer)					
	Description	Wt. %	Vol. %	Description	Wt. %	Vol. %	Sp. Gr. 20/20	Vinyl Chloride Content, Wt. %	Average Mol. Weight
M-1805	Polyethylene, Exp. low mol. wt.	100	100	—	—	—	0.92	0	14–16,000 (Soln. Viscosity)
M-2348	Polyethylene, Stand. DYNH	100	100	—	—	—	0.92	0	18–20,000 (Soln. Viscosity)
M-1364	Polyethylene Exp. high mol. wt.	100*	100*	—	—	—	0.92	0	36–38,000 (Soln. Viscosity)
M-2344	'Vinylite' VYHH Resin	98	97.5	Organo-tin heat stabilizer	2	2.5	1.36	87	55,000 (osmotic)
M-2345	'Vinylite' VYNS Resin	98	97.5	Organo-tin heat stabilizer	2	2.5	1.375	90	75,000 (osmotic)
M-2347	'Vinylite' VYNW-5 Resin	98	97.5	Organo-tin heat stabilizer	2	2.5	1.39	95	130,000 (osmotic)
M-2342	'Vinylite' VYNW-5 Resin	76.6	70	Organo-tin heat stabilizer	1.7	2.0	1.39	95	130,000 (osmotic)
				Dioctyl phthalate	21.7	28.0			
M-2343	'Vinylite' VYNW*-5 Resin	73.6	70.0	Organo-tin heat stabilizer	1.7	2.0	1.39	95	130,000 (osmotic)
				Tricresyl phosphate	24.7	28.0			
M-2346	'Vinylite' VYNW-5 Resin	76.0	70.0	Organo-tin heat stabilizer	1.7	2.0	1.39	95	130,000 (osmotic)
				Resinous Products G-25**	22.3	28.0			

Notes: *This resin contains an extremely small quantity of contaminating carbon arising in polymerization, hence, the dark gray color of molded plaque.
**Resinous type plasticizer reported to be a condensation product of sebacic acid, glycerol and ricinoleic acid.

per cent by weight of fillers and the balance is a high polymeric methyl silicone. The fillers are: 160—50 per cent zinc oxide and 50 per cent titanium oxide; 167—all titanium oxide; 180—50 per cent titanium oxide and 50 per cent silica; 181—all silica.

Omitting Melmac S-6004, a heavily filled plastic, and the filled α-Beetle, the range of volume compression under 40,000 is from .1737 for Melmac 404 to .2614 for Silicone 125-96, a range of about 50 per cent. The range of initial compressibilities is much wider than this, however. The volume compression in the first 2,500 kg/cm² varies from 0.0226 to 0.0872, a range of nearly four fold. That is, at the high pressures the initial differences tend to disappear. The silicones stand in a class by themselves, being characterized by a high initial compressibility. As already mentioned, no breaks in direction were found and the curves were all smooth. This does not mean, however, that the curves are all similar to each other, because a number of examples can be found of crossing of the curves. Any such effects are, however, not on a large scale.

The only anomaly found in all these plastics is shown by Teflon. This has, at 6,500 kg/cm², a discontinuity in volume, indistinguishable in all its traits of behavior from an ordinary reversible polymorphic transition. Since such transitions are ordinarily associated with change of lattice structure, and plastics are not, according to the ordinary point of view, endowed with a regular lattice structure, the occurrence of such a transition was unexpected. It would seem to indicate an unusually high degree of organization in the structure. Professor B. Warren, of Massachusetts Institute of Technology, was so kind as to make an X-ray analysis of a sample of teflon. He reported: "There are too many sharp lines for this to be classed as the pattern of a truly amorphous material. It is not possible to say that the material is perfectly crystalline, but it is closer to crystalline than to the completely amorphous state."

Glasses. Six glasses were measured, for which the results are given in Table II. Of these, quartz glass was from laboratory stock, selected to be free from internal striations. Pyrex was similarly selected from laboratory stock. Glasses "A," "C," and "D" are from the same rods as those used a number of years ago in measuring compressibility and the effect of pressure on rigidity (2). I owe them to the courtesy of Dr. J. T. Littleton of the Research Laboratory of the Corning Glass works. Glass "A" is a potash lead silicate of very high lead content, "C" is a soda potash lime silicate, and "D" is a lead zinc borosilicate. The borax glass I owe to the courtesy of Professor Francis Birch; it is from the same batch as that used by Dane and Birch in their measurements of the effect of pressure and temperature on viscosity (3).

Of the six glasses investigated, all but the borax glass show anomalies of one sort or another which are all beyond any possible experimental error. The anomaly of quartz glass has already been investigated (4) in another apparatus up to 50,000. It was formerly found that its compressibility increases with increasing pressure at a constantly increasing rate until a pressure of 35,000, where there is a break in the direction of the tangent (transition of the second kind in the nomenclature of Ehrenfest), and from there on decreases normally with further increasing pressure. This behavior is confirmed with the present apparatus. The discontinuity in direction is now found at a somewhat lower pressure, 31,000 instead of 35,000. The best way of seeing this is to plot the first differences of volume from Table II against pressure. With regard to absolute values, the volume decrement at 40,000 found with the present apparatus is 0.1194 against 0.1163 previously. This difference is not necessarily all instrumental, because there is reason to think that quartz glass is not a perfectly well defined substance. The anomaly of pyrex is similar in character to that of quartz glass, as is to be expected from the 81 per cent content of SiO_2 in pyrex. The break in direction is at a somewhat lower pressure for pyrex, between 28,000 and 29,000. Pyrex has been formerly measured (5) over the range up to 12,000, and the initial increase of compressibility with rising pressure

TABLE II

COMPRESSION OF GLASSES

Pressure kg/cm²	Quartz Glass	Pyrex	"A"	"C"	"D"	Borax Glass
0	.0000	.0000	.0000	.0000	.0000	.0000
5,000	.0141	.0153	.0159	.0121	.0144	.0345
10,000	.0295	.0308	.0300	.0239	.0281	.0631
15,000	.0452	.0465	.0425	.0352	.0411	.0857
20,000	.0610	.0622	.0535	.0449	.0542	.1054
25,000	.0772	.0786	.0656	.0549	.0678	.1228
30,000	.0933	.0920	.0770	.0654	.0806	.1376
35,000	.1068	.1032	.0866	.0742	.0927	.1518
40,000	.1194	.1133	.0964	.0830	.1049	.1648

found. The volume decrement at 15,000, extrapolated from the 12,000 measurements, was 0.0462 against 0.0465 found now.

Glasses "A," "C," and "D" all show the same sort of anomaly, the reverse of that of quartz glass. It is natural to ascribe this to the silicate content of these glasses. The anomaly consists in a break in the direction of the tangent, but in the direction of an increase of compressibility rather than a decrease. Above and below the break the compressibility decreases normally with increasing pressure. For glass "A" the discontinuity in $\left(\frac{\partial v}{\partial p}\right)_\tau$ occurs at 21,000 and is approximately 0.00000045 in magnitude in the units of the table; for glass "C" it occurs at 22,000 and is 0.00000055 in magnitude, and for "D" it occurs at 18,000 and has a magnitude of 0.0000004.

The anomalies in quartz glass and the silicates are thus one the inverse of the other, and would therefore seem to imply inverse mechanisms. In the case of quartz some mechanism responsible for high compressibility goes out of action on reaching a certain pressure, and in the case of the silicates some new mechanism must come into action at a critical pressure. Mechanical models are not difficult to imagine. Thus if in the case of quartz the structure contained something analogous to dished flat springs, the increase of compressibility could be explained as a geometrical effect, the spring becoming flatter the further it was compressed and therefore offering less elastic resistance because of the diminishing arching effect, and the sudden termination of the effect could be explained by the opposite sides of the dished spring being compressed into mutual contact. In the case of the silicates an analogous sort of mechanism can be imagined, only now the springs are parallel to the direction of stress and the two leaves do not begin to separate until a crucial pressure is reached. The X-ray structure of the glasses is known to be complicated enough and also to have sufficiently marked partial regularities to make it not unplausible to expect that mechanisms like these may exist.

Elements. The measurements on the elements were made both for their own sake, and also to provide the fiducial volume at 25,000 which was necessary in reducing the measurements to 100,000. These latter are reported in the previous paper; there is an overlapping range between 25,000 and 40,000 which affords a check on the measurements. The comparison of the measure-

TABLE III

COMPRESSION OF VARIOUS ELEMENTS

Pressure kg/cm²	Lithium	Sodium	Potassium	Rubidium	Caesium	Beryllium	Titanium	Zinc	Germanium	Zirconium	Lanthanum	Cerium	Praseodymium	Neodymium	Uranium
0	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000
2,500	.0204	.0334	.0677	.0696	.0999	.0024	.0027	.0040	.0040	.0026	.0100	.0109	.0090	.0078	.0024
5,000	.0389	.0624	.1152	.1224	.1585	.0047	.0052	.0079	.0078	.0054	.0194	.0234	.0174	.0152	.0048
10,000	.0715	.1115	.1862	.1982	.2392	.0094	.0099	.0154	.0152	.0111	.0370	.0549 (c)	.0329	.0289	.0095
15,000	.1005	.1511	.2374	.2506	.2981	.0139	.0143	.0225	.0213	.0168	.0526	.1655	.0471	.0416	.0139
20,000	.1261	.1856	.2772	.2920	.3442 (a)	.0181	.0185	.0293	.0268	.0220	.0665 (b)	.1864	.0604	.0536	.0181
25,000	.1485	.2111	.3093	.3254	.3908	.0219	.0224	.0358	.0323	.0267	.0827	.2027	.0729	.0650	.0219
30,000	.1689	.2350	.3360	.3530	.4261	.0256	.0261	.0420	.0375	.0312	.0952	.2154	.0848	.0757	.0255
35,000	.1872	.2559	.3584	.3760	.4559	.0294	.0297	.0480	.0426	.0356	.1072	.2257	.0961	.0858	.0290
40,000	.2040	.2740	.3774	.3954	.4816	.0329	.0332	.0537	.0476	.0399	.1189	.2342	.1069	.0955	.0324

(a) Transition at 23,300. Compressions .3716 and .3776
(b) Transition at 23,370. Compressions .0755 and .0781
(c) Transition at 12,430. Compressions .0736 and .1504

ments in the overlapping range has been anticipated in the previous paper.

The five alkali metals were from my stock, known to be of high purity. It is the same stock as that used in previous measurements (6), and reference is made to former papers foz the details of purification, etc. The caesium was freshly distilled from a glass capsule obtained from MacKay in 1937 and not opened until now. The distillation, which was slow at a minimum temperature, was necessary to remove the impurity of dissolved oxide. The details of the distillation were as in former work. For the present measurements the lithium was placed directly in the carboloy container, with no sheath of indium or other intermediary between it and the carboloy. Some misgivings were felt in doing this, because there had been previous evidence in the work to 100,000 that there might be chemical attack on the carboloy. None appeared in the present range, however, and the results should have the advantage of greater accuracy because of the absence of any second material in the piezometer. It was necessary to use a protecting sheath for the other four alkalies, however. This was made necessary both by their mechanical softness and their chemical activity. The sheath could not be made of indium or of lead, since both of these form alloys. The sofest metal which appeared feasible for the sheath was aluminum. The sheath was in the form of a double cup. The volume of the aluminum varied from 70 to 200 per cent of the alkali metal. depending on the compressibility of the metal. The various corrections, including that for the compressibility of the sheath, averaged 10 per cent of the total volume decrement.

There are previous measurements on all of these alkali metals for comparison. For lithium the volume decrement at 40,000 previously found was 0.201 against 0.204 found now. For sodium the previous decrement at 40,000 was 0.273, against 0.274 now. For potassium the respective figures are 0.375 and 0.377. For rubidium the figures are 0.431 and 0.395. This large discrepancy is doubtless the fault almost entirely of the previous measurements. These were based on measurements by the method of linear compressibility up to 12,000, a method entirely unsuitable for this material because of its excessive mechanical softness. Furthermore, the theoretical calculations of Bardeen (7) had indicated that the previous values for rubidium were out of line with what was to be expected in the direction now found. The percentage discrepancy between the former and present measurements is greatest at the low pressure end of the range. For caesium the respective figures are 0.487 and 0.482. The new figure is to be preferred. The volume discontinuity at the transition of caesium at 23,300 kg/cm^2 formerly found agrees exactly with that now found.

The beryllium I owe to Professor John Chipman of M. I. T. It was said to be of 99.7 to 99.8 purity. For further particulars the paper describing the measurements to 100,000 should be consulted. There are previous measurements (8) of the compressibility of beryllium to 12,000. These give for the volume decrement at 10,000 0.0076 against 0.0094 now found. The new value is doubtless to be preferred, because of greater purity of the present specimen. However, it must be recognized that the absolute compressibility of beryllium is so low as to restrict the accuracy obtainable with the present apparatus.

The titanium was obtained from MacKay. It was said to be of 99 per cent purity, but was hard and brittle. It is not improbable that there is a very small transition in the neighborhood of 35,000. The values given in the table are smoothed across this. There are no previous measurements for comparison. Titanium is one of the least compressible substances measured with the present apparatus, with correspondingly smaller accuracy.

The zinc was single-crystal material obtained a number of years ago from Dr. A. W. Hanson at the University of Iowa and known to be of high purity. One of the objects of measuring zinc was to find whether the indium sheath exerts an effectively hydrostatic pressure on the specimen so that the resulting measurement is one of true volume compression, and not of some other combination of the elastic constants. Since the linear compressibility of zinc is 8 times as great in one direction as the other, this is a particularly favorable material to show the effect if it exists. Three specimens were made, one with the cleavage plane perpendicular to the axis of the carboloy piezometer, one with it parallel, and one at 45°. The measurements did show a perceptible trace of the effect suspected, and in the expected direction. The volume compression on an arbitrary scale at the maximum pressure varied from 886 to 896. This is so very far from a factor of 8 to 1 that it is probably safe to assume that for most materials the stresses are sensibly hydro-

static. The figures given in the table are the average for the three orientations, and therefore possibly a trifle low. Previous measurements (9) have been made to 12,000 on the single crystal in different directions and the cubic compression calculated. The previous value at 10,000 so calculated was 0.0299 against 0.0294 found now.

The germanium I owe to the courtesy of Professor Lark-Horovitz. It has been measured to 100,000 and reference is made to that paper for further details. There are no other measurements. Over the range to 40,000 the relation between volume and pressure fails markedly of being a second-degree relation. The maximum deviation from linearity is at 12,000 instead of 20,000, and the change in direction in the general neighborhood of 12,000 is so abrupt as almost to constitute a transition of the second kind.

Zirconium was cut from a specimen obtained many years ago from Eindhoven used in previous measurements (10) to 12,000. The volume decrement formerly found at 10,000 was 0.0103 against 0.0111 found now. This is one of the more incompressible substances.

Lanthanum, cerium, praseodymium, and neodymium were all obtained from Mackay, all fresh material shipped under oil. The purity was not stated, but judging by the general appearance and mechanical softness the purity was high. Three of these metals have been measured previously (11) to 12,000 by the method of linear compressibility. The crystal system of cerium is cubic, and of the other three hexagonal close-packed. Except for cerium it was therefore not legitimate to calculate volume compression from linear compression, but in view of the close-packed character of the hexagonal structure the error was probably not large.

The compression previously found for lanthanum at 10,000 was 0.0339 against 0.0370 found now. The present value is to be preferred both because of the presumptively greater purity and also because lanthanum is not in the cubic system. The transition at 23,370 was not previously known; it runs cleanly with narrow region of indifference.

Cerium is anomalous in two respects; there is a large transition with 8 per cent volume change at 12,430, and below the transition the compressibility increases markedly with increasing pressure, the volume decrement at 10,000 being 17 per cent greater than would be given by linear extrapolation from 5,000. Previous measurements showed the same abnormal increase of compressibility, and also a transition. The transition, however, was at a much lower pressure, 7,500 kg/cm^2. It was found to be sluggish and the change of volume was not determined, the measurements having been made on a piece of wire, not an advantageous form of specimen. The transition now found was sharp and rapid. The new values are without doubt greatly to be preferred; the difference may well be ascribed to inferior purity of the former sample. A still earlier exploration of a sample of cerium with still inferior purity had disclosed no transition at all. It is, however, surprising that the pressure of the transition is so sensitive to impurity. It would indicate that the impurity forms solid solutions, and probably with both phases and with different concentrations. The previous measurements of volume compression, by linear compression of wire, were made only to 4,000 in order to avoid the effect of the transition. Extrapolation to 5,000, assuming uniform compression in all directions, of the former measurements, gives 0.0269 against 0.0234 found now. The new value is to be preferred.

In view of the anomalies of both lanthanum and cerium, increasing from lanthanum to cerium, it was somewhat of a surprise that praseodymium, the next rare earth metal after cerium, shows no anomaly whatever, but the curve is perfectly smooth. Its volume compression at 10,000, previously found, was 0.0326 against 0.0328 found now.

The curve for neodymium is perfectly smooth. There are no previous values for comparison.

Minerals. I am indebted for eleven minerals to Professor Francis Birch, who selected them from the collections of the Harvard Geology Department. Professor Birch had them ground in his machine shop by Mr. Harold Ames to the shape required for the measurements. The truncated cone form was used, and indium was placed below the specimen, between it and the stationary piston, as well as on the sides of the cone and above it, in order to ensure as close an approach to true hydrostatic pressure as possible. The specimens were all single crystals. Two specimens of orthoclase were measured; one from Madagascar was clear, and the other from Spain was opaque with small black inclusions. The olivine was gem material (peridot) from St. John's Island, Red Sea, Egypt. The diopside was from De Kalk, N. Y. The grossularite, a variety of garnet, had the indicated composition $Ca_3Al_2(SiO_4)_3$. The "garnet" was from Connecticut, and the hypersthene from Labrador.

TABLE IV

COMPRESSION OF VARIOUS MINERALS

Pressure kg/cm²	Quartz Crystal	Orthoclase Madagascar	Labradorite	Calcite	Olivine	Diopside	Grossularite	Garnet	Hypersthene	Orthoclase Spain	Halite
0	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000
10,000	.0236	.0171	.0133	.0134 (a)	.0079	.0088	.0072	.0071	.0101	.0175	.0366
20,000	.0441	.0333	.0260	.0725	.0156	.0169	.0140	.0138	.0191	.0335	.0664
30,000	.0625	.0488	.0381	.0887	.0231	.0245	.0204	.0200	.0272	.0484	.0924
40,000	.0792	.0634	.0495	.1019	.0304	.0318	.0264	.0257	.0347	.0625	.1160

(a) Two transitions

The results are collected in Table IV. There are previous measurements for a number of the minerals. For quartz, former measurements (12) to 12,000 give for the volume decrement at 10,000 0.0242 against 0.0236 found now. Extrapolating by a second degree expression to 40,000 the former measurements give a volume decrement of 0.0696 against 0.0792 actually found now. The extrapolation gives considerably too small a decrement at the high pressures; this is the usual direction of discrepancy. The two orthoclases differ little in compressibility, in spite of the great difference in appearance. Former measurements (13) to 12,000 gave at 10,000 0.0195 against 0.0171 and 0.0175 found now. Labradorite has not been previously measured. Calcite has been previously measured (14) to 50,000; in those measurements the two transitions between 10,000 and 20,000 were more carefully studied than here. In the present work the two transitions were not resolved. The former decrements at 20,000 and 40,000 were 0.077 and 0.096 respectively against 0.073 and 0.102 found now. The present results differ from the former ones in giving a greater compressibility in the range between 20,000 and 40,000. Of the remaining minerals previous measurements have been made only for halite. Previous measurements gave for the decrement at 20,000 and 40,000 respectively 0.0664 and 0.1130 against 0.0664 and 0.1160 found now. The close agreement in the results for the two varieties of garnet is to be noticed.

Substances with Transitions. Most of these were substances previously investigated (16), for which the transition parameters have been determined. There are, however, a few new ones, the transitions of which were discovered in the course of this work. Five substances with newly discovered transitions are deferred for listing in Table VII. The particular point in investigating these substances was to find the relative compressibilities of the two phases at the transition point. It had been previously found that in the majority of cases the high pressure phase, that is, the phase with the smaller volume, has the larger compressibility, a paradoxical result. The material was, in the case of those substances measured before, the same old stock, and reference is made to previous papers for a description of it. The few new materials will be described in due course. The results are shown in Table V.

The volume discontinuity of ammonium formate previously found was 0.0860 against 0.0860 found now. In general comment on the comparative volume decrements, the larger of two values is presumptively more accurate, the smaller value being due to incomplete running of the transition. This substance shows a drop in compressibility to approximately one half on passing from the low to the high pressure form.

Methylamine hydrochloride has two transitions, at approximately 5,000 and 25,000. The volume discontinuities previously found were 0.049 ± and 0.012 ± against 0.0520 and 0.0158 found now. There is no appreciable difference in compressibility of the two phases at 25,000. Not enough points were taken to determine the relative compressibility of the two low pressure phases. It is to be noted, however, that at low pressures the compressibility varies with pressure by an amount abnormally large for a solid.

The volume discontinuity of $CsMnO_4$ previously found was 0.0275 against 0.0241 now. At the transition pressure the high pressure form is approximately 11 per cent less compressible than the low pressure form.

Comparison of the present values for KCN with previous ones is not easy. It was previously found that KCN has at least four modifications. In order to obtain these, temperature was varied from dry ice temperature to 200° C. Most of the

TABLE V

SUBSTANCES WITH TRANSITIONS

Pressure kg/cm²	Ammonium Formate	Methylamine Hydrochloride	$CsMnO_4$	KCN	AgCN	PbI_2	Cu_2I_2	Urea	Thiourea
0	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000
									(i)
5,000	.0386	.0397	.0270	.0280	.0466	.0332	.0133	.0375	.0619
		(b)				(f)		(h)	
10,000	.0670	.1186	.0497	.0539	.0787	.1014	.0247	.1328	.0922
	(a)		(d)				(g)		
15,000	.1940	.1406	.0938	.0777	.1041	.1203	.0717	.1563	.1162
20,000	.2052	.1601	.1099	.0996	.1251	.1359	.0844	.1759	.1352
				(e)					
25,000	.2157	.1779	.1246	.2030	.1433	.1491	.0958	.1925	.1511
		(c)							
30,000	.2255	.2099	.1384	.2166	.1594	.1604	.1064	.2066	.1650
35,000	.2348	.2251	.1516	.2287	.1741	.1712	.1164	.2188	.1776
40,000	.2438	.2398	.1644	.2402	.1879	.1810	.1260	.2295	.1893

(a) Transition at 11,420; Volume decrements .0742 and .1853
(b) Transition at 5,530; Volume decrements .0436 and .0956
(c) Transition at 25,270; Volume decrements .1790 and .1948
(d) Transition at 13,430; Volume decrements .0643 and .0884
(e) Transition at 20,340; Volume decrements .1011 and .1885
(f) Transition at 5,150; Volume decrements .0369 and .0761
(g) Transition at 14,400; Volume decrements .0339 and .0702
(h) Transition at 5,490; Volume decrements .0411 and .1053
(i) Transition at 3,540; Volume decrements .0309 and .0512

TABLE V (Continued)

SUBSTANCES WITH TRANSITIONS

Pressure kg/cm²	Nitrourea	Semicarbazide Hydrochloride	Quinone	Guanidine Sulfate	d-Camphor	Ammonium Pentaborate	Potassium Pentaborate	Dextrose Sodium Iodide	$MgSO_4 7H_2O$
0	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000
			(l)	(m)	(o)		(q)		
5,000	.0354	.0276	.0611	.1757	.1365	.0360	.0754	.0263	.0235
	(j)	(k)							
10,000	.1156	.0525	.0997	.1951	.1712	.0606	.0977	.0494	.0445
				(n)					(u)
15,000	.1383	.0708	.1300	.2161	.1962	.0806	.1171	.0697	.0844
20,000	.1570	.0864	.1552	.2284	.2158	.0984	.1337	.0880	.0999
						(p)	(r)		
25,000	.1725	.0998	.1763	.2388	.2319	.1378	.1549	.1045	.1139 (v)
									.1412 (v)
30,000	.1861	.1119	.1943	.2480	.2456	.1529	.1666	.1196	.1539
								(s)	
35,000	.1981	.1229	.2095	.2565	.2577	.1646	.1767	.1489	.1644
								(t)	
40,000	.2088	.1332	.2224	.2647	.2694	.1741	.1858	.1693	.1747

(j) Transition at 5,510; Volume decrements .0387 and .0911
(k) Transition at 9,470; Volume decrements .0469 and .0501
(l) Transition at 4,530; Volume decrements .0477 and .0568
(m) Three transitions below 5.000.
(n) Transition at 10,460; Volume decrements .1968 and .2027
(o) Transition at 3,540; Volume decrements .0748 and .1229
(p) Transition at 23,300; Volume decrements .1092 and .1317
(q) Transition at 3,540; Volume decrements .0211 and .0663
(r) Transition at 20,340; Volume decrements .1348 and .1411
(s) Transition at 30,220; Volume decrements .1202 and .1364
(t) Transition at 37,190; Volume decrements .1542 and .1622
(u) Very sluggish transition between 10,000 and 15,000.
(v) Probably two sluggish transitions in neighborhood of 25,000. Volume discontinuity of one about four times that of other.

transitions are fast, but at low pressures and high temperatures there is one transition so sluggish that it could not be brought down to room temperature, and furthermore there was evidence at the higher temperatures of the capricious appearance of an absolutely unstable form. The present measurements gave evidence only of the high pressure transition, in the neighborhood of 20,000. This ran unusually sharply, and all the measurements on this substance were unusually good, the difference between readings with increasing and decreasing pressure being unusually small. However, the volume change at the transition was now found considerably smaller than the previous value, 0.0874 against 0.102. The atmospheric density, calculated from the absolute position of the piston, was high, 1.64 against 1.52 given in I. C. T. It is perhaps not inconceivable that on the initial seasoning application of pressure a small amount of the absolutely unstable phase appeared and maintained itself. This is consistent with a larger than usual permanent change of volume after the seasoning application. The present results show a 23 per cent drop of compressibility on passing through the transition from the low to the high pressure form.

No evidence for a transition of AgCN was found in the present work. Previously a sluggish transition with very small volume change, 0.001, was found in the neighborhood of 14,000.

The volume discontinuity previously found for PbI_2 was larger than that found now, 0.049 against 0.039. The transition comes at such a low pressure that the change of compressibility on passing through the transition could not be established.

The former and the present transition parameters for Cu_2I_2 agree very closely; the pressures are indistinguishable and the volume discontinuity was 0.0360 against 0.0363 now. There is a 35 per cent increase of compressibility on passing through the transition to the high pressure phase. The transition of thiourea has been previously studied, but only at temperatures of 100° or above. Extrapolated to 25° the former measurements would give 3,460 for the transition pressure and 0.0139 for the discontinuity of volume against 3,540 and 0.0203 given above. The transition pressure is too low to permit a determination of the relative compressibility of the two phases.

Previous measurements on nitrourea disclosed no certain transition. However, the pressure exploration was combined with high temperatures and it appeared that there were complex decomposition phenomena. It is probable that the transition was missed in the former work because of some irreversible transformation of the substance. In the present work a clean transition with 5 per cent volume change was found near 5,000. Any discontinuity of compressibility on passing through the transition is too small to be established.

In previous work on semicarbazide hydrochloride the measurements were confined to temperatures of 75° or higher because the transition was too sluggish at lower temperatures. In the present measurements at room temperature the transition was very sluggish, running at 15,400 with increasing pressure and 3,540 with decreasing pressure. Within these pressure limits the curves with increasing and decreasing pressure were parallel, indicating no appreciable difference of compressibility between the low and high pressure phases. The mean transition pressure of the present work, 9,470, is markedly higher than the 5,500 extrapolated from previous work. The extrapolated volume discontinuity is about ten times that given in the table. Comparison of measurements with so sluggish a transition is not significant.

The transition parameters obtained for quinone with the present apparatus are in much doubt, the transition limits being 4,000 kg/cm² wide. The former determinations were also in doubt, no determinations of volume discontinuity being attempted below 75° because of sluggishness of the transition. The former volume discontinuity extrapolated is 0.0370 against 0.0091 found now. Allowing maximum uncertainty to the extrapolation there would seem to be little doubt that the present volume discontinuity is too small. The present results give no sufficient evidence as to a discontinuity of compressibility at the transition.

Guanidine sulfate has three transitions below 5,000 which run so sluggishly that a slow change of volume continues for some time after pressure has been released and the apparatus disassembled. No attempt was made to resolve these transitions, but reference is made to the previous work. There is also a sluggish transition near 10,000 for which a volume discontinuity of 0.0059 was found in the present work against 0.0071 formerly. It seems probable, although not certain, that there is a moderate increase of compressibility on passing to the high pressure form through the transition at 10,000.

The transitions of d-camphor have been studied in two previous papers. The phase diagram is

the most complicated of any substance yet investigated, there being probably eleven modifications up to 35,000. A number of these are sluggish and run only at elevated temperatures. In the present work the complicated change which starts with modification II and ends with III, perhaps passing through IV and V as intermediate forms, was found to run at a mean pressure of 3,540 against 2,700 formerly. The present over-all change of volume is 0.048 against 0.053 formerly. The former work indicates by extrapolation that a transition from III to VIII should run at room temperature in the neighborhood of 13,000. No evidence for this was found in the present work, the transition apparently being totally suppressed by sluggishness at the low temperature. This means that the compression data given in the table above the transition pressure pertain to the modification III. The data would indicate a drop of compressibility to nearly one half on passing from II to III.

Ammonium perborate has not been previously measured. I owe it to the courtesy of Dr. Hans Jaffe of the Brush Development Co. It was provided in single crystal form, and had been produced as part of the war time program of investigation of all possible piezo-electric crystals. My intention was to measure it in my program of linear compressibility measurements up to 30,000. Discovery of transitions, however, made it impossible to use for this purpose. This substance in all probability has two transitions instead of the one shown in the table. Below 5,000 there is probably a small transition with volume discontinuity of the order of one seventh of that given in the table at higher pressures. Both transitions are sluggish. The volume discontinuity associated with the transition at 23,000 is probably too small and the compressibility immediately above the transition too high. The data as given in the table indicate a jump up of compressibility on passing to higher pressures through the transition, and an abnormally rapid dropping of the compressibility of the high pressure phase with increasing pressure.

Potassium pentaborate, like ammonium pentaborate, has not been previously measured. It was obtained from the same source, for the same purpose, and like it had to be discarded for measurement of the linear compressibility because of transitions. It also has two transitions, but inversely situated as compared with ammonium pentaborate. Here the larger transition is at the low pressure, and one with volume discontinuity only one seventh as large at the high pressure. The sluggishness is not as great as for the ammonium salt. At the high pressure transition there is no appreciable discontinuity of compressibility. There may be a slight upward jump in compressibility on passing to the high pressure form at 3,540, although this is not certain.

Dextrose sodium iodide I owe to the courtesy of Dr. S. O. Morgan of the Bell Telephone Laboratories. It was single crystal stock, destined for measurement of the linear compressibility in the 30,000 apparatus. Two transitions were found, both above 30,000, so that it was possible to measure the linear compressibility over the entire range up to 30,000 in addition to the present measurements of volume compression to 40,000. Reference is made to a following paper for the details of the linear compressions in different directions. The volume compression at 30,000 calculated from the linear compressions was 0.1183 against 0.1196 found now.

The $MgSO_4$ $7H_2O$ I owe to the kindness of Mr. George C. Kennedey, who grew it from aqueous solution by the method of slowly lowering temperature. It was destined for measurements of the linear compression up to 30,000, but the discovery of the complicated system of transitions indicated in the table prevented measurements of linear compression above 10,000. At 10,000 the volume compression calculated from the linear compressions was 0.0408 against 0.0445 given in the table. It is probable that the lower value is more accurate, the present measurements being obscured by the sluggish transition.

Miscellaneous Compounds. Compounds 1 to 8 in Table VI were obtained from the Eastman Kodak Co., from their commercial stock. Of these numbers 1 to 5 were tried because they have multiple carbon bonds, and it was thought that there was some possibility that such compounds might suffer irreversible transitions at sufficiently high pressures similar to that found in CS_2. None was found, however. I owe the suggestion of which compounds of this nature would be most feasible to try to Dr. Linus Pauling.

Compounds 9 to 25 were single crystal stock, destined to be used in the measurements of linear compression to 30,000. Full details about the origins of this material will be found in a paper to follow this. Comment here is required on only two of these materials. $NiSO_4$ $6H_2O$ has a very marked transition of the second kind in the direction perpendicular to the axis in the neigh-

TABLE VI

VOLUME DECREMENTS OF MISCELLANEOUS COMPOUNDS

Pressure kg/cm²	1 Melamine	2 Cyanamide	3 Di Cyanamide	4 Hexamethylenetetramine	5 Oxalic Acid anhydrous	6 2–4-Dichlorophenol	7 Iodoform	8 Urea Nitrate	9 Ammonium Phosphate	10 Potassium Phosphate	11 Sulfamic Acid	12 $Li\,Na_2\,Cr_4O_7\,6H_2O$	13 $NaCl\,O_3$
0	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000
5,000	.0376	.0357	.0340	.0433	.0357	.0549	.0549	.0372	.0177	.0179	.0207	.0172	.0185
10,000	.0618	.0615	.0589	.0739	.0620	.0893	.0921	.0642	.0332	.0335	.0378	.0345	.0349
15,000	.0811	.0832	.0796	.0976	.0835	.1149	.1194	.0855	.0471	.0474	.0524	.0490	.0491
20,000	.0975	.1019	.0976	.1167	.1010	.1358	.1414	.1034	.0595	.0599	.0654	.0620	.0616
25,000	.1116	.1184	.1138	.1330	.1161	.1533	.1599	.1191	.0709	.0713	.0775	.0753	.0736
30,000	.1242	.1334	.1285	.1474	.1296	.1687	.1759	.1331	.0815	.0817	.0885	.0883	.0854
35,000	.1358	.1471	.1421	.1599	.1421	.1823	.1902	.1456	.0914	.0912	.0970	.0995	.0952
40,000	.1469	.1600	.1547	.1708	.1538	.1945	.2034	.1569	.1006	.0996	.1050	.1083	.1031

TABLE VI (Continued)

VOLUME DECREMENTS OF MISCELLANEOUS COMPOUNDS

Pressure kg/cm²	14 Rochelle Salt	15 Potassium Alum	16 $Ni\,SO_4\,6H_2O$	17 Sodium Ammonnium Tartrate	18 Rubidium Tartrate	19 Morpholine Hydrogen Tartrate	20 Ammonium Dihydrogen Phosphate	21 Ethylene Diamine Tartrate	22 Dextrose Sodium Chloride	23 HCO_3	24 Benzil	25 Strontium Formate
0	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000
5,000	.0235	.0282	.0174	.0271	.0234	.0333	.0170	.0290	.0266	.0264	.0605	.0180
10,000	.0439	.0514	.0340	.0498	.0435	.0596	.0322	.0523	.0490	.0459	.0961	.0344
15,000	.0616	.0704	.0477	.0692	.0607	.0812	.0459	.0718	.0684	.0625	.1243	.0491
20,000	.0770	.0869	.0596	.0863	.0758	.0995	.0585	.0886	.0861	.0770	.1480	.0621
25,000	.0920	.1020	.0739	.1014	.0894	.1155	.0700	.1033	.1025	.0898	.1676	.0741
30,000	.1053	.1157	.0870	.1148	.1014	.1298	.0806	.1161	.1178	.1015	.1838	.0856
35,000	.1167	.1281	.0979	.1267	.1120	.1424	.0904	.1273	.1320	.1123	.1978	.0958
40,000	.1262	.1393	.1070	.1372	.1214	.1536	.0999	.1372	.1452	.1225	.2102	.1052

borhood of 20,000, the compressibility increasing abruptly at this pressure. The same anomaly is shown also by the volume measurements of Table VI, but quantitatively it is not nearly as large as would be demanded by the length measurements. It would appear that this anomaly does not become fully developed when the stress is not truly hydrostatic. The second material is benzil, which showed a complicated system of anomalies for the length measurements, but no trace of them in the volume measurements of Table VI. Again, part at least of the anomaly would seem to be suppressed by comparatively light constraint.

Compounds with Ortho-, Meta-, and Para- Forms. A study was made of a large number of compounds of this class to find whether there is any systematic variation in compressibility. The compounds were selected from the catalogue of the Eastman Kodak Co., all the groups for which the three forms were listed and for which all three are solid under ordinary conditions. The results are collected in Table VII. There are a few groups for which only two forms are tabulated; in these groups three forms had been listed and ordered but one of the forms proved to be out of stock. The purity is that usual to chemicals of this nature, and is indicated in the catalogue. In a few cases grades of "technical" or "practical" purity only were available; these are indicated in the following. As furnishing some clue to the character of the material, the densities at atmospheric pressure and room temperature are also recorded in the table. These densities were obtained incidentally in the course of the measurements from the weight and the absolute dimensions at atmospheric pressure of the charge when mounted in the piezometer.

The arrangement in the table is a sort of hybrid alphabetical arrangement, according to the most important part of the molecule.

Of the compounds, o- and m- amino phenol were listed as "practical" grade, and m-phenylene diamine as "technical." The m-chloroacetanilide was marked on the bottle "to contain 5 per cent of an aromatic amine"; the di-m-cresyl carbonate contained an appreciable quantity of some sort of moisture which squeezed out when the pellet for the piezometer was formed, and the tri-m-cresyl thiophosphate contained so much visible moisture that it did not seem worth while to measure it. It should be noticed incidentally that the para form of the sodium-xylene-sulfonate is not similar in structure to the other two,

TABLE VII

COMPRESSIONS OF ORTHO-, META-, AND PARA- COMPOUNDS

	1			2			3			4			5			6			7		
Pressure kg/cm²	Chloroacetanilide C_8H_8ONCl			Nitro-aniline $C_6H_6O_2N_2$			Diphenyl Benzene $C_{18}H_{14}$			Nitro-chloro-benzene $C_6H_4O_2NCl$			Nitro-bromo-benzene $C_6H_4O_2NBr$			Nitro-iodo-benzene $C_6H_4O_2NI$			Amino-Benzoic Acid $C_7H_7O_2N$		
	o	m	p	o	m	p	o	m	p	o	m	p	o	m	p	o	m	p	o	m	p
0	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000
2,500	.0347	.0311	.0259	.0228	.0240	.0255	.0339	.0294	.0314	.0333	.0328		.0320	.0253	.0266	.0310	.0268	.0271	.0265	.0160	.0271
										(a)											
5,000	.0610	.0572	.0477	.0421	.0438	.0457	.0609	.0536	.0561	.0673	.0584		.0556	.0456	.0488	.0544	.0489	.0493	.0479	.0292	.0483
													(b)								
10,000	.0998	.0971	.0822	.0729	.0748	.0772	.1012	.0918	.0934	.1113	.0963		.0991	.0774	.0843	.0893	.0825	.0835	.0814	.0503	.0808
15,000	.1297	.1261	.1084	.0964	.0991	.1018	.1303	.1199	.1195	.1386	.1237		.1292	.1018	.1105	.1152	.1077	.1087	.1064	.0671	.1058
20,000	.1540	.1490	.1292	.1149	.1190	.1217	.1526	.1414	.1394	.1591	.1455		.1513	.1214	.1312	.1355	.1276	.1290	.1267	.0809	.1262
25,000	.1740	.1678	.1463	.1305	.1357	.1385	.1708	.1591	.1557	.1752	.1633		.1687	.1377	.1487	.1522	.1438	.1460	.1433	.0928	.1431
30,000	.1901	.1832	.1603	.1439	.1498	.1532	.1856	.1739	.1698	.1890	.1785		.1833	.1517	.1638	.1664	.1577	.1607	.1573	.1034	.1578
35,000	.2034	.1960	.1714	.1559	.1620	.1662	.1982	.1865	.1823	.2005	.1916		.1956	.1637	.1770	.1797	.1699	.1733	.1691	.1130	.1707
40,000	.2144	.2066	.1803	.1669	.1733	.1777	.2091	.1973	.1937	.2107	.2031		.2061	.1741	.1887	.1916	.1811	.1846	.1793	.1221	.1821
Atmospheric Density	1.349	1.337	1.335	1.465	1.434	1.446	1.171	1.195	1.247	1.558	1.512		1.943	1.982	1.952	2.304	2.171	2.198	1.346	1.526	1.371

(a) Transition at 4.030. Compressions .0484 and .0550. (b) Transition at 7.490. Compressions .0741 and .0795

TABLE VII (Continued)

COMPRESSIONS OF ORTHO-, META-, AND PARA- COMPOUNDS

Pressure kg/cm²	8 Chloro-Benzoic Acid $C_7H_5O_2Cl$			9 Bromo-Benzoic Acid $C_7H_5O_2Br$			10 Iodo-Benzoic Acid $C_7H_5O_2I$			11 Methyl- — -Nitro-cinnamate $C_{10}H_9O_4N$			12 Di- — -cresyl carbonate $C_{15}H_{14}O_3$			13 Amino Phenol C_6H_7ON			14 Nitro-Phenol $C_6H_5O_2N$		
	o	m	p	o	m	p	o	m	p	o	m	p	o	m	p	o	m	p	o	m	p
0	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000
2,500	.0275	.0288	.0273	.0266	.0308	.0263	.0275	.0266	.0257	.0301	.0290	.0273	.0365	.0340	.0312	.0267	.0239	.0236	.0317	.0258	.0271
5,000	.0494	.0514	.0494	.0482	.0544	.0473	.0495	.0487	.0471	.0532	.0512	.0492	.0623	.0606	.0553	.0467	.0429	.0423	.0563	.0462	.0488
10,000	.0829	.0862	.0832	.0812	.0914	.0804	.0824	.0834	.0819	.0887	.0855	.0836	.1007	.0991	.0913	.0774	.0728	.0725	.0935	.0780	.0834
15,000	.1084	.1124	.1088	.1061	.1190	.1053	.1066	.1093	.1082	.1148	.1117	.1096	.1286	.1267	.1174	.1016	.0955	.0965	.1211	.1024	.1095
20,000	.1288	.1330	.1293	.1261	.1408	.1257	.1266	.1302	.1290	.1358	.1327	.1305	.1504	.1483	.1380	.1209	.1137	.1159	.1419	.1222	.1304
25,000	.1456	.1502	.1465	.1431	.1588	.1430	.1430	.1474	.1465	.1532	.1504	.1477	.1676	.1663	.1551	.1364	.1287	.1323	.1589	.1385	.1474
30,000	.1599	.1646	.1612	.1577	.1739	.1577	.1568	.1623	.1616	.1682	.1655	.1625	.1816	.1814	.1692	.1493	.1413	.1465	.1728	.1525	.1621
35,000	.1728	.1776	.1741	.1706	.1869	.1706	.1688	.1750	.1749	.1813	.1785	.1755	.1932	.1945	.4811	.1604	.1521	.1590	.1846	.1646	.1748
40,000	.1848	.1897	.1856	.1822	.1980	.1823	.1800	.1857	.1864	.1938	.1903	.1870	.2031	.2060	.1911	.1703	.1613	.1705	.1947	.1750	.1861
Atmospheric Density	1.530	1.516	1.511	1.916	1.840	1.871	2.211	2.138	2.173	1.401	1.396	1.416	1.243	1.284	1.265	1.279	1.255	1.287	1.481	1.476	1.468

TABLE VII (Continued)

COMPRESSIONS OF ORTHO-, META-, AND PARA- COMPOUNDS

Pressure kg/cm²	15 Phenylene-diamine $C_6H_8N_2$			16 Phenylene-diamine Hydrochloride $C_6H_{10}N_2Cl$			17 Amino Benzene Sulfonic Acid $C_6H_7O_3NS$			18 Sodium- — -Xylene Sulfonate $C_8H_{11}O_4SNa$				19 Tri- — -Cresyl Thio-phosphate $C_{21}H_{21}O_4P$		20 Toluic Acid $C_8H_8O_2$			21 Acetyl- — -Toluidine $C_9H_{11}ON$			22 Toluidine Hydrochloride $C_7H_{10}NCl$		
	o	m	p	o	m	p	o	m	p	o	m	p	m p + $1H_2O$	o	p	o	m	p	o	m	p	o	m	p
0	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000		.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000
2,500	.0255	.0253	.0267	.0183	.0227	.0153	.0221	.0188	.0197	.0206	.0236	.0195		.0320	.0364	.0329	.0305	.0328	.0284	.0324	.0280	.0240	.0328	.0229
									(c)															(e)
5,000	.0468	.0465	.0482	.0340	.0403	.0281	.0402	.0323	.0544	.0391	.0440	.0354		.0563	.0643	.0583	.0539	.0588	.0519	.0582	.0503	.0416	.0588	.0774
10,000	.0809	.0797	.0811	.0601	.0673	.0493	.0683	.0523	.0958	.0706	.0775	.0609		.0929	.1041	.0945	.0896	.0975	.0874	.0995	.0843	.0684	.0976	.1073
									(d)															
15,000	.1070	.1053	.1061	.0835	.0893	.0669	.0898	.0676	.1320	.0959	.1029	.0814		.1196	.1333	.1216	.1168	.1255	.1134	.1308	.1097	.0899	.1261	.1288
20,000	.1279	.1253	.1257	.1050	.1080	.0824	.1076	.0798	.1563	.1165	.1229	.0987		.1410	.1558	.1430	.1387	.1476	.1341	.1550	.1298	.1075	.1485	.1460
25,000	.1450	.1412	.1417	.1237	.1246	.0959	.1223	.0902	.1736	.1342	.1390	.1137		.1587	.1741	.1609	.1567	.1664	.1509	.1743	.1458	.1226	.1668	.1608
30,000	.1596	.1544	.1555	.1399	.1394	.1079	.1356	.0997	.1868	.1492	.1524	.1261		.1739	.1895	.1763	.1725	.1825	.1653	.1899	.1599	.1359	.1817	.1741
35,000	.1720	.1656	.1675	.1536	.1523	.1186	.1473	.1087	.1979	.1617	.1638	.1369		.1874	.2025	.1900	.1861	.1962	.1783	.2032	.1722	.1479	.1946	.1861
40,000	.1825	.1756	.1779	.1648	.1634	.1284	.1578	.1172	.2076	.1722	.1737	.1467		.1998	.2137	.2023	.1976	.2079	.1897	.2147	.1829	.1587	.2065	.1972
Atmospheric Density	1.229	1.223	.1259	1.424	1.378	1.493	1.617	1.668	1.478	1.476	1.492	1.498		1.293	1.419	1.309	1.232	1.296	1.162	1.138	1.169	1.247	1.216	1.191

(c) Transition at 3,980. Compressions .0270 and .0376.

(d) Transition at 11,440. Compressions .1058 and .1082.

(e) Transition at 2,550. Compressions .0234 and .0551.

but contains one molecule of water of crystallization.

There is a great range in the mechanical properties of these compounds, and these properties might well be studied for their own sake. Most of the compounds form smooth and compact pellets when subjected to the preliminary pressure of the order of 15,000 kg/cm², but there are a few exceptions in which the pellet is extremely friable and difficult to handle. Notably in this class were the three sodium-xylene-sulfonates. The pellet in these cases can be made coherent enough to get into the piezometer by greasing the mold in which it is formed with a minimum amount of a mixture of vaseline and colloidal graphite. Sometimes merely rubbing the internal wall of the steel mold with graphite was sufficient.

In general the mechanical strength of these compounds is so low that one can expect the effect of the initial configuration, whether as powder or flakes or granules, to vanish from the final measurements, which should give very closely the true cubic compression of single crystal material under hydrostatic pressure. Direct check was made of this for o-chloro benzoic acid, which showed no significant difference between a pellet formed by fusing and turning to shape and a pellet formed in the regular way by compression of the dry powder.

Certain features of the behavior of various of the substances require detailed comment. There is an increase of compressibility of about 30 per cent on passing through the transition of o-nitrobenzene from the low to the high pressure form. There is an increase of compressibility of 65 per cent on passing from the low to the high pressure form of o-nitrochlorobenzene, and the compressibility of the latter form decreases abnormally rapidly with increasing pressure immediately above the transition point. There is an enormous increase of compressibility on passing to the high pressure form at the low pressure transition of p-amino-benzene sulfonic acid, the exact magnitude of which is difficult to estimate because of the low pressure range of stability of the low form. The second form drops rapidly in compressibility with increasing pressure above the transition. At the second transition the compressibility also jumps up on passing to the high pressure form. This substance is one which exhibited extreme friability and friction in the formation of the pellet; there may well have been a connection with the low pressure transition. The transition listed for p-toluidine hydrochloride was unusually sluggish and ran perceptibly over a pressure range of 20,000 kg/cm² with increasing pressure, and the reverse transition with decreasing pressure required an unusually long time for completion at atmospheric pressure. The compressions in the first 20,000 kg/cm² cannot be expected to be very accurate, but may be expected to be obscured by transition effects. The data given in the table for o-phenylene diamine hydrochloride are smoothed so as to completely ignore a small initial episode at low pressures in some respects like a transition, but largely irreversible. It is also to be noticed that the compressibility of this substance decreases linearly with pressure above 20,000, instead of at a continually retarded rate, as for most all other substances in the table. Finally, m-phenylene-diamine was the only substance which during compression exhibited any effects indicative of friction or failure of approximate hydrostatic pressure. This snapped twice audibly on increase of pressure, and at one point there was a slight discontinuity in piston displacement. The behavior on release of pressure was normal. This material is unusually glass-like and brittle.

In order to give a general idea of the nature of the results for these compounds, the compressions at the top pressure, 40,000, are plotted in Figure 1 for the different members of the various series of compounds, including in the compressions the transitions in the five cases in which they occur. It is evident at a glance that there is no systematic effect of the o-, m-, p- structure on compression, although there are many instances where the differences of compression between the different forms are large. Statistically, the ortho form is the most compressible of the three in 9 cases, and least compressible in 6; the meta form is most compressible in 6 and least compressible in 8 cases; and the para form most compressible in 7 and least compressible in 8 cases. Considering the small number of examples this distribution must be judged to be completely random. The abnormally small compression of the meta forms of amino-benzoic acid and amino-benzene sulfonic acid is to be commented on. In view of the very large variations in these two series it must be recognized that on occasion other factors than o-, m-, or p- position may be much more potent in determining compressibility. It would be rewarding to make an X-ray analysis of these two amino compounds to find whether there is anything unusual about the crystal structure.

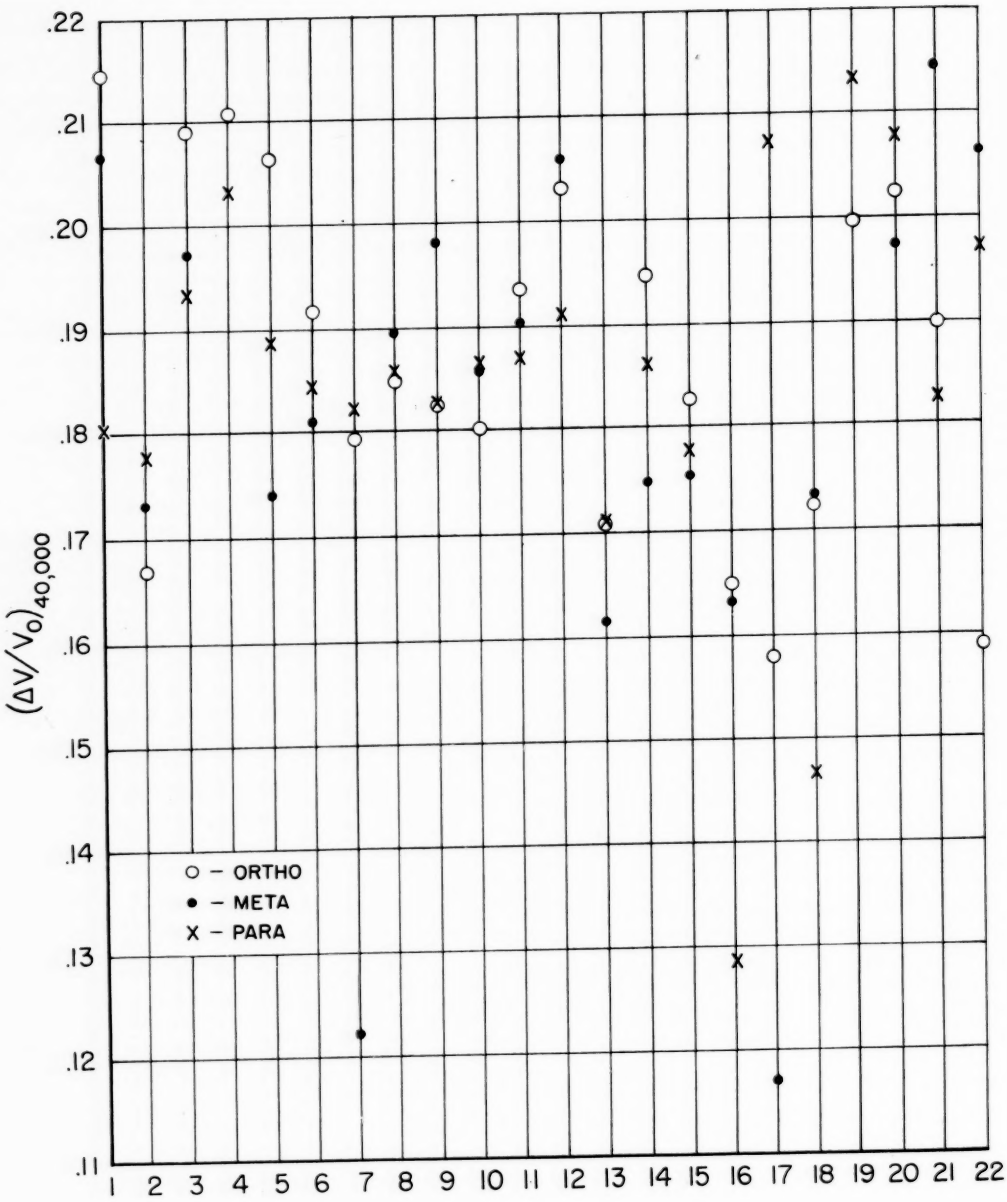

FIGURE 1. The relative compressions at 40,000 kg/cm² of the various series of o-, m-, and p- compounds as numbered in Table VII.

Other things being equal, it is to be expected that the compressions in any single series of compounds will be in the inverse order of the densities at atmospheric pressure. In order to see to what extent the density controls, I have compared the order of the inverse compressions with that of the atmospheric densities for all 22 series of compounds, and find the same order for the two properties in only 5 of the 22 instances. This is hardly more than would be expected by pure chance, so that the conclusion may be drawn that the connection is not immediate and unique between density and compression. There is however, a recognizable statistical connection. If one plots the product of atmospheric density and relative compression at 40,000 instead of merely relative compression at 40,000 in a diagram analogous to figure 1, it will be found that the three points for any one series have an obvious tendency to bunch much more closely than in figure 1.

It might perhaps be expected that at pressures as high as 40,000 any specific effects of structure might tend to be wiped out, leaving outstanding the contribution to the compression of the atoms themselves. In this case, one might expect some approach to an additive law of compression in terms of atomic constitution. In order to facilitate examination of this question the gross overall atomic formulas of the various compounds have been given in Table VII. I have not, however, been able to find any significant correlation, suggesting the conclusion that the intrinsic compressibility of the atoms entering into these compounds differs so little that any effect of them is obscured by other factors. It might be mentioned, however, that the two series differing only by the substitution of one halogen for another, namely the series 4, 5, 6 and 8, 9, 10 of the table, do show the same progression of values in the product of atmospheric density and compression at 40,000, a progression not shown by the compressions themselves. The variation of the product within any single series is, furthermore, comparatively minor.

The shape of the curves of volume decrement against pressure is in general the same for the three members of a series. There are, however, several examples of crossing of the curves, which means a different variation of compressibility with pressure for the different forms. Among the most pronounced of these instances are: m- and p- diphenyl benzene, o- and p- phenylene diamine, and o- and m- phenylene diamine hydrochloride. The apparent example of o- and m- dicresyl carbonate is uncertain, because of probable impurity of the m- form, a perceptible amount of liquid having been squeezed out on formation of the pellet.

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